Green and Sustainable Polymers: High-Value Aliphatic Polycarbonates from CO_2 and Epoxides



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ABBREVIATIONS AND SYMBOLS

Abbreviation or Symbol	Signification
^{13}C-NMR	13-Carbon Nuclear Magnetic Resonance
^{1}H-NMR	Proton Nuclear Magnetic Resonance
Cat.	Catalyst
CHO	Cyclohexene Oxide
CO_2	Carbon Dioxide
cPC	Cyclic Propylene Carbonate
D	Polydispersity
DMAP	4-(N,N-dimethyl)aminopyridine
DSC	Differential Scanning Calorimetry
EO	Ethylene Oxide
HH	Head-to-Head Sequence Arrangement
HT	Head-to-Tail Sequence Arrangement
IR	Infrared Spectroscopy
M_n	Number Average Molecular Weight
mol-%	Molar Percentage
M_w	Weight Average Molecular Weight

NMR	Nuclear Magnetic Resonance
OAc	Acetate Group [CH_3-(C=O)-O]
PCHC	Poly(cyclohexene carbonate)
PO	Propylene Oxide
PPC	Poly(propylene carbonate)
PPO	Poly(propylene oxide)
ROP	Ring-Opening Polymerisation
Salophen	General Class of Bis(salicylaldimine) Ligands and Complexes
TBA	Tetrabutyl Ammonium
TBA-Cl	Tetrabutyl Ammonium Chloride
TBA-OAc	Tetrabutyl Ammonium Acetate
T_g	Glass Transition Temperature
THF	Tetrahydrofuran
T_m	Melting Temperature
TOF	Turnover Frequency
TON	Turnover Number
TT	Tail-to-Tail Sequence Arrangement

CHAPTER 1

INTRODUCTION

1.1 SYNTHETIC POLYMERS

Polymeric materials of the air? The realisation of this dream is an enormous challenge for many scientists and researchers all over the world.

Synthetic polymers are utilised in nearly every part of modern life, e.g. as packaging material, in building and construction business, clothing, automotive industry, agriculture, electric and electronic industry and other every day purposes. One reason for this wide application field is their effortlessness in fabrication and moulding. Other reasons are their advantages in material properties compared to former materials like stone, wood, metal, glass or natural rubber. It is possible to synthesise polymers in a very economic way with a low weight and friction, with a very high strength and toughness or with a resistance against abrasion and corrosion. Hence, it is not surprising that polymers have outstripped or even displaced the traditional materials in so many application areas.

One critical handicap for today's plastics industry is the big dependence on fossil raw materials. The most common industrial polymers like polyethylene, polypropylene, polystyrene and many others are formed out of 100% of crude oil. The political unstable situation in Middle East and the undependable delivery from Russia lead to permanent fluctuating prices for natural resources. Thus, it involves an unpredictable financial risk for the industry. Another problem with serious consequences displays the fact, that the global crude oil resources are limited. Calculations of the year 2006 show that there are approximately 175 billion tons of fossil crude oil left (Table 1).

	Crude oil resources	Production	Consumption
OPEC countries	122.490	1.635	347
OECD countries	38.488	1.162	1.915
Others	14.406	1.124	1.576
Total	**175.384**	**3.921**	**3.838**

Table 1 **Expected numbers of crude oil resources, production and consumption in million tons (for 2005).**[1]

It is obvious that if the actual annual consumption of about 3.8 billion tons will be retained unchanged, fossil fuel reserves will be exhausted within the next 50 years. This clarifies the importance and inevitability of the development of alternative forms of energy and new concepts for the synthesis of new materials, which are at the moment predominately based on carbon gained from natural resources. Otherwise a life on today's standard will not be feasible anymore.

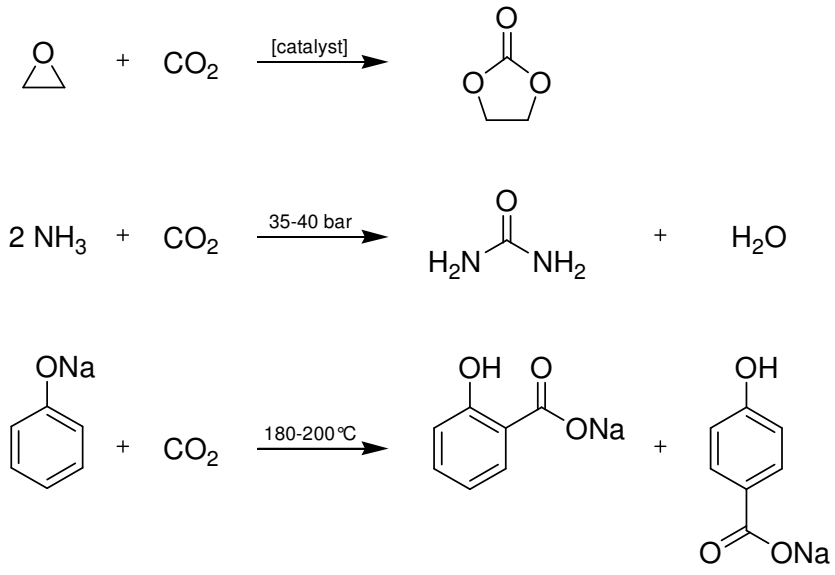
One attractive way to handle this problem could be the utilisation of carbon dioxide as a renewable C1 building block. Recovered CO_2 can be used for producing chemicals, fuels, plastics and other useful products. There are numerous reviews and books on various aspects of CO_2 utilisation.[2,3,4,5,6,7,8] There are several motivations for producing chemicals from CO_2 whenever possible:

A) CO_2 is a totally renewable feedstock compared to crude oil or coal. **B)** Carbon dioxide is a cheap and non-toxic building block that can often replace toxic chemicals like phosgene or isocyanates.[9] **C)** The production of chemicals from CO_2 can lead to totally new materials such as polymers described in the following chapters. **D)** New routes to existing chemical intermediates and products could be more efficient and economical than current methods.[10,11] **E)** The production of chemicals from CO_2 could have a small but significant positive impact on the global carbon balance.

Carbon dioxide is generally considered to be a green, or environmentally benign, solvent and reactant that is cheap, non-toxic, non-flammable and naturally abundant.[12,13] As such, CO_2 has been suggested as a sustainable alternative for organic solvents in various chemical processes.[14,15] While CO_2 is certainly not a panacea, it shows several characteristics which propose the use of CO_2 providing both economic and environmental benefit.

1.2 COMMERCIAL PROCESSES USING CARBON DIOXIDE

There are already three important industrial processes with carbon dioxide as starting material: the synthesis of cyclic carbonates, urea and salicylic acid (Scheme 1). Carbon dioxide also could be used more widely as a solvent. For example, supercritical CO_2 (the state existing at 31°C and 73.8 bar) offers advantages in terms of stereochemical control, product purification and environmental issues in the fabrication of fine chemicals and pharmaceuticals. Approximately 110 million tons of carbon dioxide are currently used for chemical synthesis per year. The majority (90 x 10^6 tons) is consumed in the industrial production of urea (mainly used as fertilizers and resins).[16] In addition to these commercial applications of CO_2 as a C1 feedstock, several challenging operation sequences involving the chemical fixation of carbon dioxide are under intensive investigation. The most promising processes are the methanol and formic acid syntheses and the production of polymers, especially aliphatic polycarbonates.



Scheme 1 **Carbon dioxide as starting material in the synthesis of cyclic carbonates, urea and salicylic acid.**

In addition to these commercial processes using carbon dioxide, several promising reactions are currently under investigation in various laboratories. These reactions differ in the extent to which CO_2 is reduced during the chemical transformation.[17]

1.3 BARRIERS TO FURTHER DEVELOPMENT

For the utilisation of carbon dioxide as a building block to produce chemicals and fuels, there are a lot of technical, economic and social barriers. To make decisions on potential ways to deal with these circumstances, information is needed concerning: **A)** The magnitude of environmental consequences. **B)** The economic costs of these consequences. **C)** Options available that could help avoid or diminish the damage to our environment and the economy. **D)** The environmental and economic consequences for each of these options. **E)** An estimate of cost for developing the technology to implement these options. **F)** A complete energy balance which accounts for energy-demanding steps and their costs.

Economic barriers to carbon dioxide utilisation can be associated with introduction of new products, the properties of which are unknown, introduction of new processes for existing products and shortage of complete life cycle analyses for production of many chemicals. Polycarbonates produced by copolymerisation of carbon dioxide and epoxides are examples of new polymeric materials. As catalysts for these reactions improve, focus is shifting from the technical obstacles associated with production to potential markets for these new materials. The situation is not unlike that encountered with the first production of polymers that are currently used on large scales. Similarly, if alternative processes to produce existing products are found, their introduction may be slow due to the large capital investments already made in current processes. For example, the production of polyurethanes from carbamates (derived from CO_2) could be economically and environmentally attractive. However, this process may not be commercialised because of competition with existing processes which have incurred large capital investments. Finally, methods that allow complete life cycle analyses of competing synthetic strategies must be developed. Analyses must include economic and environmental costs as well as the conservation of materials. It is possible that a process using CO_2 as a feedstock could actually produce more CO_2 than one not using CO_2. Full life cycle analysis should permit quantitative evaluation of how much CO_2 is avoided

by one process versus another. These analyses must also include the possibility of replacing fossil energy sources with non-fossil sources.[18]

Significant barriers exist in every area of carbon dioxide utilisation. For the synthesis of fuels and chemicals, many barriers are common and progress will require a better understanding of reaction mechanisms and thermodynamics of reaction intermediates. A deeper investigation of reactions including CO_2 leading to the cleavage of C-O bonds as well as the formation of C-C, C-H and C-X bonds is an essential need. For example, the mechanism for the cleavage of C-O bonds during the reduction of CO_2 is still not understood very well. Haltiwanger et al. showed that for the electrochemical reduction of CO_2 to CO mediated by a palladium catalyst, a free coordination site at the metal is necessary to facilitate the C-O bond cleavage.[19] This cleavage occurs via migration of a hydroxide (after protonation of the coordinated CO_2) from a metal carboxylate carbon atom to a free coordination site on the palladium. Another kind of C-O bond cleavage appears via the formation of MC(O)OM' intermediates.[20] So far, the energetic differences between possible pathways are not understood and should be clarified by theoretical calculations. In many cases, CO_2 binding occurs via both, the carbon and the oxygen atom. In order to improve reactions including the incorporation of carbon dioxide, these cooperative interactions should be studied in more detail.

1.4 NEW APPLICATIONS

One promising project for the utilisation of carbon dioxide is the reduction of CO_2 to formic acid. Rayner et al. at the University of Leeds, are working on the improvement of this catalytic process.[21] Formic acid has potential to power fuel cells for electricity generation in small, portable electronics such as phones and laptop computers and as a precursor for other fuels and commodity chemicals, including polymers.[22] For the conversion hydrogen is necessary, which could be a drawback, but compared with using methanol or hydrogen alone, formic acid seems to have the greater potential. One advantage of formic acid is that it does not interpenetrate the polymer membrane of the fuel cell, so its efficiency can be higher than that of methanol. Another advantage is the lower toxicity compared with methanol, making it a somewhat safer fuel in case of leakage.

Another promising investigation was done by Li et al.[23] They found a new way for the synthesis of cyclic carbonates. In this new process CO_2 and olefins are directly converted into cyclic carbonates with water as solvent. Cyclic carbonates are useful and often greener substitutes for toxic phosgene and dimethyl sulfate in many chemical reactions. They also serve well as solvents, especially in medicine and cosmetics, and they are electrolytes of choice in lithium-ion batteries. The compounds are readily prepared from CO_2 and epoxides (as described on page 4, Scheme 1) but preparing the epoxide is an extra step that could be avoided. So the direct synthesis of cyclic carbonates from simple olefins instead of epoxides is an easier and cheaper reaction. This synthesis also contributes to the goal to eliminate wastes from purification steps as well as to avoid the production of phosgene or chlorine, which are by-products in the formation of epoxides. There are several additional advantages of this reaction. First, using water as solvent is a benefit compared with using an organic solvent. Next, an expensive metal catalyst or metal oxidising reagent is not needed, as the oxidation can be catalysed by using an ammonium bromide salt, an amine base and hydrogen peroxide (H_2O_2). Bromine reacts with the olefin in water to form a bromohydrin intermediate (containing bromine and hydroxyl substituents). The base subsequently deprotonates the hydroxyl group to form an alkoxide that

attacks CO_2 to form the cyclic carbonate. The peroxide serves to reoxidise bromide ions to complete the catalytic cycle, leaving water as the only by-product.

One very attractive and maybe promising activation and utilisation of carbon dioxide was shown by Antonietti et al. They introduced a mesoporous graphitic carbon nitride as a heterogeneous, metal-free catalyst for Friedel-Crafts reactions.[24,25] Recently, they showed that this catalyst can also chemically activate carbon dioxide.[8] They postulated that in the first step of the catalytic process, CO_2 binds to individual free amino groups present in the carbon nitride. This step leads to the formation of a carbamate species. The formed carbamate would then be well positioned to react with an aromatic molecule (like benzene) activated by the catalyst. Formally, CO_2 is split into an $O^{\cdot\cdot}$ diradical, which is consumed by the oxidation of benzene to phenol and carbon monoxide. The latter is available for subsequent reactions involving the formation of C-C bonds for synthesis of organic structures. In biological photosynthesis, the energy for CO_2 splitting is not provided by a substrate, but by photons. It is thus very attractive to ask whether their simple chemical model could be a first step towards artificial photosynthesis (i.e. the formation of organic compounds and oxygen from CO_2).

Using CO_2 directly as a chemical feedstock is not the only option for possible applications. Carbon dioxide can be converted to carbon monoxide, which can be used in a host of organic syntheses. Its most established use is the utilisation as a component of synthesis gas (a mixture of CO and H_2), which is an important feedstock for the chemical industry for making methanol or hydrocarbon fuels (biodiesel) via Fischer-Tropsch reactions. An overview of transition-metal complexes which mediate electron transfer in the photochemical reduction of CO_2 is given by Fujita et al.[26] Designing photo-catalyst systems that use solar energy to reduce carbon dioxide to hydrocarbons means nothing else than making the so called “artificial photosynthesis” possible.

DuBois et al. worked on another example of the attempt to chase after nature’s methods of capturing CO_2. So far, they developed bimetallic palladium catalysts with triphosphine ligands that reduce CO_2 to carbon monoxide.[27] Because

palladium is expensive, it's a further challenge to switch to a nickel-based catalyst to make large-scale reduction of CO_2 feasible.

There are limited numbers of commercial examples where CO_2 is used as a reaction solvent. One of the most notable is its utilisation in the manufacture of fluoropolymers (which previously relied on chlorofluorocarbons which are no longer available after their environmental impact was realised).[28] In addition, Thomas Swan Ltd. in the United Kingdom has a commercial continuous flow reactor for large-scale reactions, particularly hydrogenations and alkylations.[29] Reactions involving light gases (hydrogen, carbon monoxide and oxygen) have been the subject of intensive studies because of their total miscibility with supercritical CO_2 compared to their only limited solubility in conventional solvents.[30,31,32,33,34]

Trends in Electrochemical Carbon Dioxide Reduction

The electro-reduction of CO_2 at various metal electrodes yields all kinds of organic substances, like methane, ethane, carbon monoxide, ethanol and other alcohols. Sánchez et al. summarised representative results for the direct electrochemical CO_2 reduction at solid electrodes.[35] The entity of electro-catalytic behaviour among metals can be grouped into *sp* and *d* metals.[36] The electro-reduction techniques had overcome the difficulty of finding electrodes with both a high electro-catalytic activity and a satisfactory lifetime. Also, because of the relatively low solubility of CO_2 in aqueous solutions methods for improving its solubility had to be found. A possible solution of this problem is to perform the electro-reduction at high pressure or in non aqueous solutions.

Jitaru et al. showed a summary of the most important methods for the electrochemical reduction of CO_2 on flat metallic cathodes via a novel classification system.[37] The new classification system gives a better understanding of the relationship between the electro-reduction product and the nature of the metallic electrode or supporting electrolyte. Similar reduction products are formed by each of the four possible combinations of electrodes and supporting electrolytes (*sp* group metals in aqueous and non-aqueous electrolyte

and *d* group metals in aqueous and non-aqueous electrolyte, respectively). The discussion has included both synthetic aspects and mechanistic considerations.

The difference between the electro-catalytic behaviour of electrodes made of *sp* group metals or *d* group metals, respectively, was recognised as an important criterion in determining the selectivity of electrode processes.[38,39] Several classification systems have been used to systemise the impressive number of data accumulated in CO_2 related synthetic work.[40] Most of these classifications are merely based on the nature of the main product obtained in the electrochemical synthesis. Four classes of metallic electrodes in aqueous solutions supporting electrolytes and three classes for non-aqueous media can be distinguished. Thus in aqueous solution: **A)** Metallic In, Sn, Hg and Pb are selective for the production of formic acid. **B)** Metallic Zn, Au and Ag produce carbon monoxide. **C)** Metallic Cu exhibits a high electro-catalytic activity for the formation of hydrocarbons, aldehydes and alcohols. **D)** Metallic Al and Ga show low electro-catalytic activity in CO_2 reduction. In non-aqueous supporting electrolytes: **A)** On Pb, Tl and Hg the main product is oxalic acid. **B)** On Cu, Ag, Au, In, Zn and Sn carbon monoxide and carbonate ions are obtained. **C)** Al and Ga form both carbon monoxide and oxalic acid.

The main competitive reactions involve species with hydrogen atom participation. Thus, in the electrochemical reduction of CO_2 in water, hydrogen formation competes with the CO_2 reduction reaction. Therefore, the suppression of hydrogen formation is very important because the applied energy is wasted on hydrogen evolution instead of being used for the reduction of CO_2.

1.5 SUSTAINABILITY

During the past few decades, the concept of sustainable development has gained considerable authority as a directive principle in the scientific community. The 1987 WCED report *"Our Common Future"*, better known as the Brundtland Report, defines sustainable development as "meeting the needs of the present without compromising the ability of future generations to meet their own needs".[41,42]

This concept of sustainability dictates that not only the availability of natural resources and the capacity of the environment to cope with human activities should be taken into account. Also the limitations set by the current state of technology and the future developments therefore are an essential part in the realisation of the concept of sustainable development. From that point of view chemical engineering and process technology are key-disciplines at the interface of an expanding and demanding market of consumers on the one side and a concerned and suspicious society on the other. This implies that both scientists and engineers should focus on the development. At the same time it satisfies and anticipates the needs of present and future generations. In that respect, the process discussed in this thesis contributes to sustainable development for three different reasons: **A)** The chemistry of this process allows the production of polycarbonates without requiring unfavourable chemicals such as phosgene. **B)** Carbon dioxide, a renewable resource that is often treated as waste, is effectively converted into a useful product. **C)** The suggested production process does not require solvents and, consequently, prevents the possibility of solvent losses to the environment. The contribution of this process to sustainable development can even be further increased by expanding the currently limited range of applications of these polymers. Possibly, herein lies a major challenge and most promising opportunity.

1.6 THEME AND CONTENT OF THE THESIS

Prior to this work, fundamental investigations on the alternating copolymerisation of carbon dioxide (CO_2) and epoxides were performed in our group.† Thus, the present work was focused on the improvement of known and the development of new catalytic systems. The main intention was not only to optimise the properties of the polymer and the polymerisation efficiency, but also to determine a model for the reaction mechanism. The prior insufficient understanding of the mechanism, and further more the inefficiency of the available catalysts prevented the production of attractive aliphatic polycarbonates in industrial scale. Today, the amplified understanding of mechanistic details enables the synthesis of improved catalysts and led to the development of new concepts for the formation of aliphatic polycarbonates.

The alternating copolymerisation of CO_2 and propylene oxide (PO) is of high interest for the industry because it enables an excellent technique for the application of cheap and industrially available building blocks. The utilisation of cheap monomers is, in addition to highly active catalysts, an essential factor for the realisation of industrial fabrication.

The reaction of carbon dioxide with metal complexes has been extensively studied, revealing potential pathways for catalytic reactions. However, the thermodynamic stability of CO_2 has hindered its convenience as a reagent for chemical synthesis. To overcome this limitation, reactions applying CO_2 with very reactive reagents have been investigated. Especially the catalytic coupling with heterocycles has received extensive attention over the past three decades.[43,44,45] Reactions of carbon dioxide are dominated by nucleophilic attacks on the carbon, which result in bending the O-C-O angle to approx. 120°. Generally, energy must be supplied to drive the desired conversion. Thus, high temperatures, high pressures, extremely reactive reagents, electricity or the energy from photons may be exploited to carry out carbon dioxide reactions.

† Cooperation with BASF Aktiengesellschaft, Ludwigshafen

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CHAPTER 2

MONOMERS

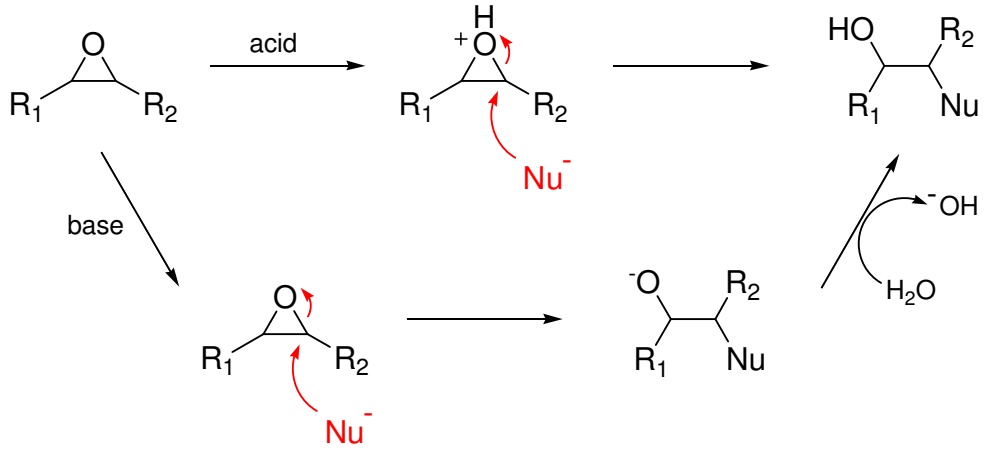
2.1 CARBON DIOXIDE

The fixation of carbon dioxide by green plants using solar energy is the most important chemical process running on earth. The last report of the "*Intergovernmental Panel on Climate Change"* (IPCC) calls carbon dioxide the most important anthropogenic greenhouse gas.[1] The global atmospheric concentration of carbon dioxide has increased from a pre-industrial value of about 280 ppm to 379 ppm in 2005. The atmospheric concentration of CO_2 in 2005 exceeds by far the natural range over the last 650.000 years (180 to 300 ppm) as determined from ice cores. The annual CO_2 concentration growth-rate was larger during the last 10 years (1995 – 2005 average: 1.9 ppm per year), than it has been since the beginning of continuous direct measurements (1960 – 2005 average: 1.4 ppm). The primary source of the increased atmospheric concentration of carbon dioxide since the pre-industrial period is the use of fossil fuel and, but in a minor way, the change of land-use.

Within the growing concern about the environmental impact of chemical substances, the possibility of recycling carbon dioxide from industrial emissions and of removing some of this greenhouse gas has received increasing attention as a potential carbon source in the synthetic chemical industry.[2,3,4] Likewise, the possibility of using CO_2 as the starting material for the synthesis of fine chemicals provides an attractive alternative to compounds presently derived from petroleum.[5] CO_2 is generally considered as a green, environmentally benign solvent and reactant that is cheap, non-toxic, non-flammable and renewable.[6,7] Atmospheric carbon dioxide is an abundant (750 billion tons in atmosphere), but diluted source of carbon (only 0.036 % by volume).[8] The utilisation of CO_2 could even result in more economical and/or more efficient procedures of existing applications.[9,10] Moreover, the production of chemicals and polymers including CO_2 might lead to new materials.

2.2 EPOXIDES

An epoxide (oxirane) is a cyclic ether with only three ring atoms. This ring is an approximately equilateral triangle, i.e. its bond angles are about 60°, which makes it highly strained. The strained ring makes epoxides more reactive than other ethers, especially towards nucleophiles (Scheme 1).



Scheme 1 **Acid or base catalysed addition of a nucleophile to an epoxide.**

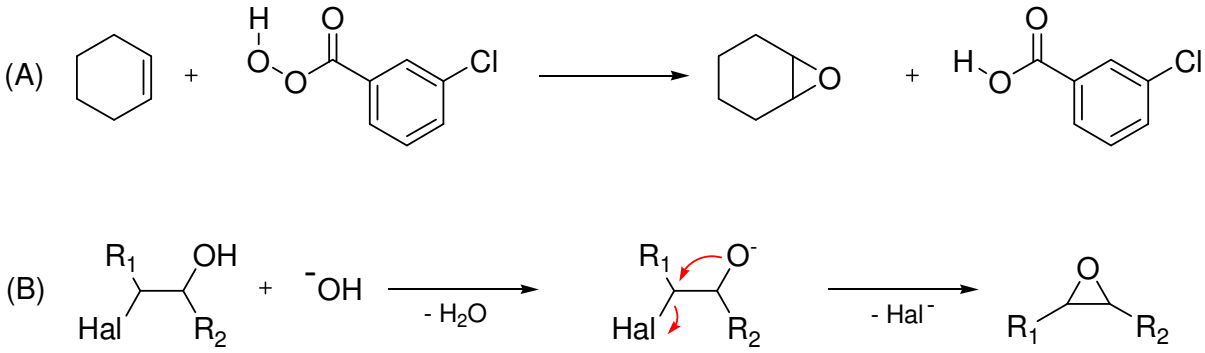
Because of the enormous angle strain in this small ring, epoxides undergo acid or base catalysed C–O bond cleavage more easily than larger ring ethers.

1) Acid catalysed cleavage of epoxides: A) The oxygen of the epoxide is protonated by the acid. **B)** The protonated epoxide is attacked by weak nucleophiles such as water or alcohol. **C)** The more hindered carbon is attacked due to the carbocation character that the protonated epoxide possesses.

2) Base catalysed cleavage of epoxides: A) A base such as $^{-}$OH, $^{-}$OR or Grignard reagent attacks the least hindered carbon in an S_N2 fashion. **B)** The alkoxide that results from the S_N2 attack is protonated.

Preparing Epoxides

There are two main routes to synthesise epoxides (Scheme 2): **(A)** Reaction of an alkene with a percarboxylic acid. **(B)** The intramolecular S_N2 reaction of a 1,2 halohydrin (a halogen is next to an alcohol). When treated with a base the alcohol is deprotonated. The resulting alkoxide attacks the vicinal carbon, eliminating the halogen and forming the epoxide.



Scheme 2 Two methods for the synthesis of epoxides.[11]

The interest in epoxides results from their ease in preparation and their usefulness as a reactive functional group that can provide a variety of products after treatment with either electrophilic or nucleophilic reagents. The simplicity of opening the strained three-membered ring of epoxides with attack of reagents in a stereospecific manner results in either one or two stereochemical products (when applicable), usually in good yield. The use of epoxides in organic chemistry is quite extensive, they are used to prepare monomers, prepolymers, polymers and copolymers.[12]

Ethylene oxide (EO) and propylene oxide (PO) are the two most important epoxides for industry; for this reason, they are readily available in industrial scale. After the Second World War the development of the petrochemical industry led to the large-scale production of ethylene oxide and propylene oxide. Most synthetic routes are based on the oxidation of carbon double bonds with oxygen or peroxides. The most important commercial process involves the direct air oxidation of an olefin over a silver catalyst.[13] The primary use of ethylene oxide is as an intermediate in the production of several industrial chemicals,

most notably, ethylene glycol. Ethylene glycol is used primarily in automotive antifreeze. Polyester is used in fibres, films and bottles. A small fraction of the total consumption is used for the disinfection and sterilisation of foodstuffs and medical equipment.

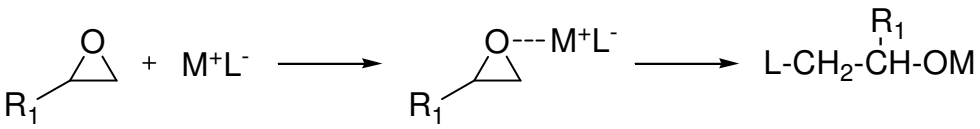
More than 6 million tons of propylene oxide were produced in the USA, Western Europe, Japan and several other countries in 2005.[14] Propylene oxide is used mainly (60%) as an intermediate in the production of polyurethane polyols, which are used to make polyurethane foams, coatings and adhesives. Further 20% of PO are applied in the manufacture of propylene glycol, which is used in fibre-reinforced plastics, foods, cosmetics, pharmaceuticals, cigarette tobacco, packaging materials and hydraulic fluids. Smaller amounts of PO are needed in the preparation of glycol ethers (3%), dipropylene glycol (2%), industrial polyglycols, lubricants, surfactants, oil demulsifiers, isopropanolamines, as a solvent and soil sterilant (6%).

2.3 HOMOPOLYMERISATION OF EPOXIDES

Epoxides are fairly reactive organic compounds especially when compared with the relatively inert carbon dioxide molecule. When oxiranes are used as a co-monomer in polycarbonate synthesis, the difference in reactivity can result in the formation of polyethers (homopolymerisation of epoxides) due to an undesired side reaction. Because this homopolymerisation can be a seriously competing reaction, this unwanted process is described first.

In 1863, Wurtz was one of the first researchers who achieved to make macromolecules via the oligomerisation of epoxides.[15] About 60 years later, Levene reported the first successful polymerisation of epoxides.[16]

There are three main ring-opening reactions for the polymerisation of epoxides: Acid (cationic), base (anionic) and coordinative initiation. Acid and base initiated reactions are shown in chapter 1, page 4, Scheme 1. Ionic coordinative polymerisation involves a complex of a metal (M) such as Al, Cr, Fe, etc., with ligands (L) (e.g. OH, OR, Cl) that coordinates in an ionic manner with the oxygen atom of the epoxide. The complexation is followed by nucleophilic attack of the ligands, which results in opening the oxirane ring to give initiated species that can undergo propagation to form the polymer chain (Scheme 3).



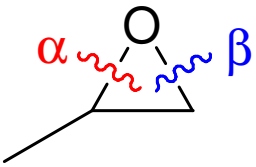
Scheme 3 Coordinative polymerisation of epoxides.[17]

2.3.1 STEREOCHEMISTRY

In case of asymmetric epoxides (e.g. propylene oxide) as monomers in a (co)polymerisation reaction, the stereochemistry of the obtained polymers has a large influence on the polymer properties, such as its melting point and crystallinity. The stereochemical aspects of these ring-opening polymerisations (ROPs) are very similar to the ones found in the polymerisation of α-olefins (e.g. propylene, 1-hexene, styrene, etc.). The regio and stereo isomerism observed in the polymerisation will be explained in the following paragraphs with poly(propylene oxide) (PPO) as an example.

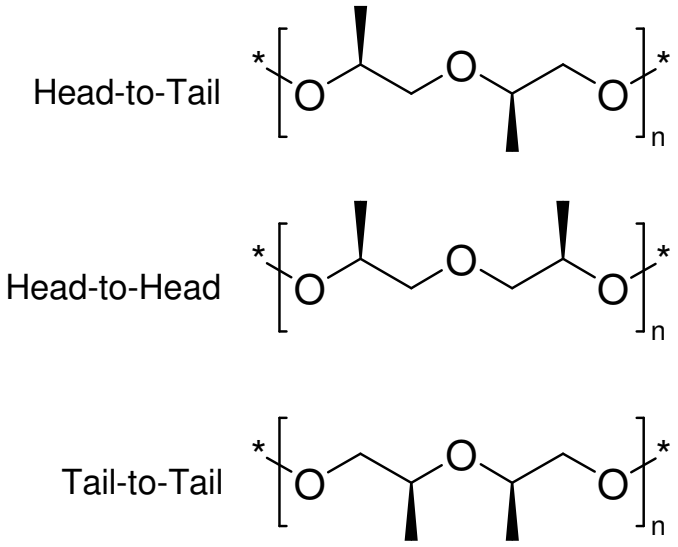
2.3.2 REGIO ISOMERISM

For asymmetric oxiranes, the bond cleavage for the ring-opening can occur at two different places. It can either be between the methyl substituted carbon and the oxirane oxygen (α) or between the methylene group and the oxygen atom of the epoxide (β) (Scheme 4).[18]



Scheme 4 **Ring-opening of propylene oxide.**

(Co)polymerisation of asymmetric epoxides can result in (co)polymers with different regio isomers as depicted in Scheme 5. ^{13}C NMR as shown by Hamaide et al. can easily identify these different isomers.[19]



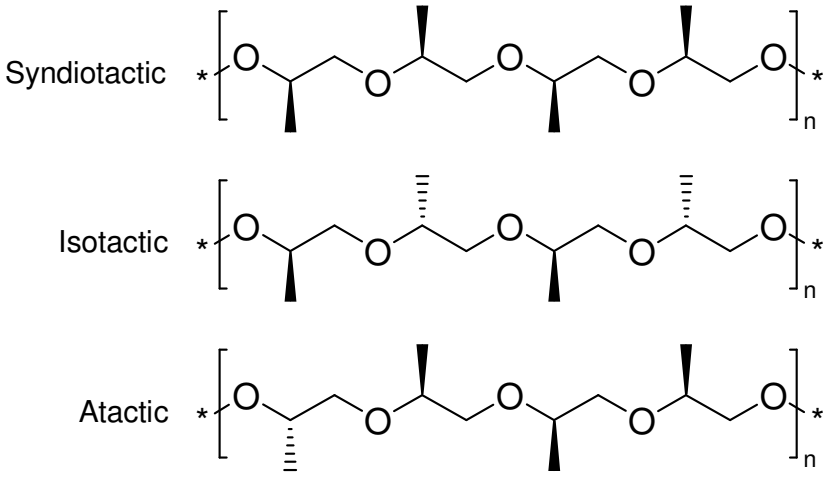
Scheme 5 Regio isomers of poly(propylene oxide).

Usually an asymmetric monomer has a preferred direction to incorporate into a growing chain. Monomers like propylene, styrene or vinyl chloride have a strong preference for head-to-tail incorporation. For epoxides, this preference is much lower and leads to an increase of head-to-head and tail-to tail units in the polymer chain. Usually ring-opening takes place at the less hindered β-carbon atom.

2.3.3 STEREO ISOMERISM

Another type of isomerism is stereo isomerism. Propylene oxide exists in both the R- and S-optical form and the stereochemistry of the obtained polymers can be described in terms of tacticity (Scheme 6). If all monomer units have the same optical configuration, the polymer is said to be isotactic. When monomer units have an alternating inverted optical configuration, the polymer is said to be syndiotactic. When the optical configuration is completely random, an atactic polymer is obtained.

In order to achieve an isotactic polymer, one option is to use only one enantiomer of the monomer, which is expensive, or to use a racemic mixture of chiral catalysts.[20]

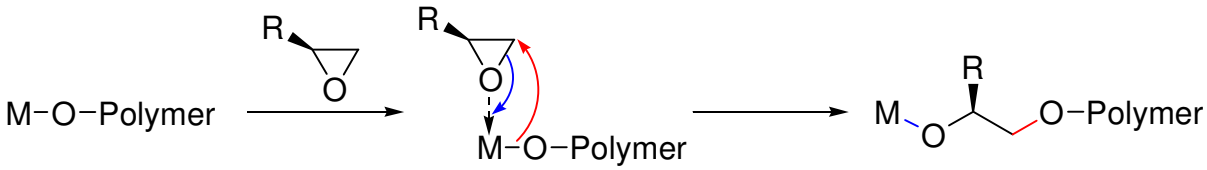


Scheme 6 **Tacticity of poly(propylene oxide).**

Two types of stereochemical control exist: **A)** Chain end control, the growing chain induces selective incorporation of a monomer.[21] **B)** Enantiomeric site control, the enantioselective incorporation is induced by ligands around the catalytic active metal centre.[22]

2.3.4 COORDINATION MECHANISM

The following section gives an overview of the homopolymerisation of epoxides with coordination type catalysts. In a coordination mechanism, the propagation step occurs at the metal centre by insertion of a pre-coordinated monomer in the metal-alkoxide bond of the growing chain (Scheme 7). This mechanism is comparable to the polymerisation mechanism encountered in catalytic olefin polymerisation, in which a pre-coordinated olefin inserts into a metal-carbon bond.



Scheme 7 **Coordination mechanism in the homopolymerisation of epoxides.**

One of the first catalyst systems, able to polymerise epoxides through a coordination mechanism, was a $FeCl_3$/PO system.[23] The most commonly used types of coordination catalysts are dialkyl zinc and trialkyl aluminium compounds in conjunction with alcohol or water. Compared to cationic or anionic polymerisation, these systems offer several advantages: The polymers formed via a coordination mechanism generally have higher molecular weights. A coordination mechanism also has the potential to control the stereochemistry of the polymers because the propagation step occurs at the metal centre and the ligand system can influence the orientation of the polymer chain and the monomer.

Unfortunately, most catalyst systems are only able to generate polymers with isotactic diad contents of about 40-70%.[24,25] Another disadvantage is the rather low rate of polymerisation compared to the anionic or cationic polymerisation. An example of a commercial process using a coordination catalyst system is the ring-opening polymerisation of PO with a calcium amide/alkoxide catalyst.[26,27]

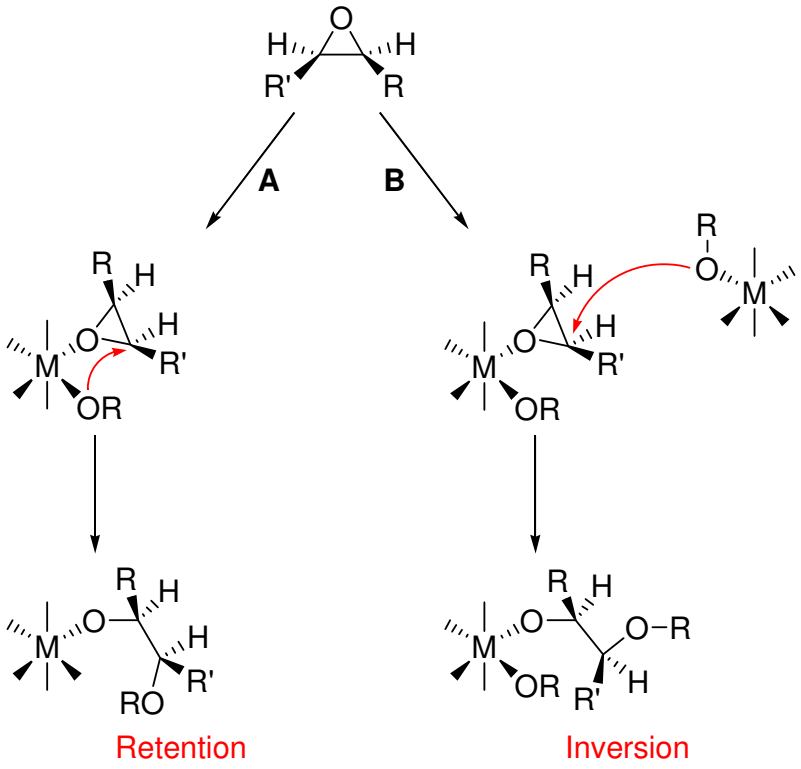
Initiation

Initiation of the polymerisation requires a vacant coordination orbital at a Lewis acidic metal centre and a reactive bond in which the epoxide can insert. This is usually a metal-alkoxide bond. The initial formation of a catalyst-epoxide adduct can be a very exothermic reaction and can generate a lot of heat. Barron et al. found that sometimes the initial preparation of an epoxide adduct under controlled conditions is required to prevent overheating of the polymerisation mixture, as is the case with an $FeCl_3$ catalyst.[24]

Propagation

When a 1,2-bis-substituted monomer is used, the stereochemistry of the carbon atom, where the ring-opening takes place, depends on the type of coordination mechanism. Propagation can occur at either a single metal centre (pathway **A**) or at two separate metal centres (pathway **B**) as depicted in Scheme 8.[28,29] Pathway **A** involves a migratory insertion of the monomer, similar to the

mechanism of the olefin polymerisation, while the stereochemistry of the chiral methine carbon with the R' substituent is retained.[30,31,32] In pathway **B**, a second metal centre activates the monomer and the nucleophilic attack of the polymer chain occurs at the other side of the monomer inducing an inversion of stereochemistry at the methine carbon. When a bimetallic metal complex is involved, where the metal centres are in close vicinity to each other, nucleophilic attack is more likely to take place at the same side of the monomer (retention).

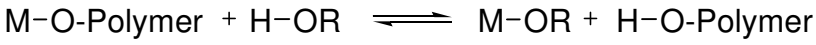


Scheme 8 **Propagation steps of the coordination mechanism involving either single (pathway A) or multiple (pathway B) metal sites.**

In contrast to the widely applied anionic polymerisation of propylene oxide, a coordination mechanism induces a larger amount of inverted insertions (regio isomerism); i.e. insertion after a ring-opening of the α-bond (Scheme 4, page 23). This can be explained by the enhanced polarisation of the α-bond due to the Lewis acidic metal centre. In addition, an electron-donating methyl group can stabilise the partial positive charge after ring-opening. The amount of inverted insertions was studied in detail by M.-F. Llauro et al. by ^{1}H and ^{13}C NMR

spectroscopy. They used several aluminium and rare earth alkoxides for the polymerisation of propylene oxide.[18]

During the generally living polymerisation reactions only one chain per catalytic active centre is produced. Therefore, a chain transfer reagent (usually an alcohol) is often used to control molecular weight (Scheme 9).[33] This reversible reaction is used to induce the so-called “immortal” polymerisation. It is called “immortal” since re-initiation and further polymerisation of the chain end remains possible after termination with a protic species like methanol or water.[34] The termination leads to polymers with hydroxyl chain ends, which can also act as another chain transfer reagent. A big advantage is the possibility to have a good control over the polymerisation process.



Scheme 9 Schematic representation of a chain transfer reaction.

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CHAPTER 3

POLYCARBONATES

3.1 INTRODUCTION

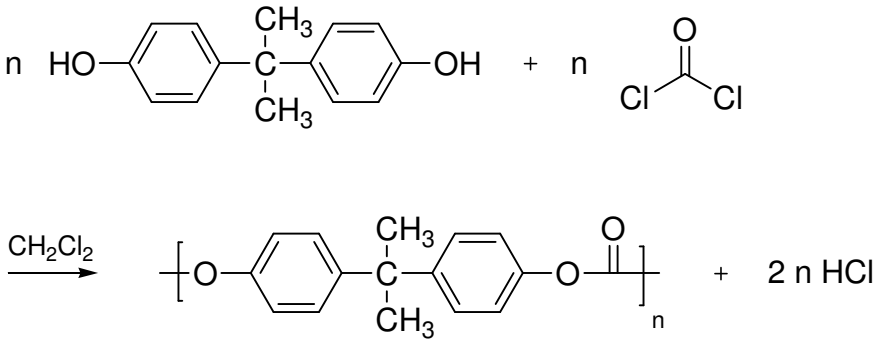
Polycarbonates are amorphous polymers with excellent material properties. They incorporate many excellent attributes of metals, glasses and synthetics like transparency, rigidity, high impact resistance and heat-deflection temperature (up to 148°C).[1] Associated with multiple converting possibilities, they are deployed as high-quality plastics. The application area extends from insulating foils to compact discs. The first who achieved to synthesise high molecular polycarbonates was Hermann Schnell by *Farbenfabriken Bayer AG* in 1953.[2] This polymer based on 2,2-bis-(*p*-hydroxyphenyl)propane (bisphenol-A).

Polycarbonates are divided into two fields, the poly(aromatic carbonate)s and the poly(aliphatic carbonate)s.

3.2 AROMATIC POLYCARBONATES

The aromatic polycarbonates obtained from bisphenol-A are the industrial thermoplastics with the second largest volume of sales. The annual volume of these polymers exceeds 1 million tons.[3] They are plastics with very attractive engineering properties including good dimensional stability, low moisture absorption (0.12%) and high impact strength (izod notched impact strength up to 90 kJm^{-2}) coupled with high light transmission (up to 88%) and good electrical insulation values (volume resistivity 10^{14} Ωm).[4] The most common members of aromatic polycarbonates are Makrolon® from Bayer AG, Lexan® from General Electric and Calibre® from Dow Chemicals. One important application is their use as the material for compact discs and DVDs. Another brought application area is based on its characteristics like low weight, high impact resistance and optical properties. Thus, it is the material of choice for the utilisation as alternative for window glasses in the automotive industry and building sector as well as for eyeglass lenses or motorbike crash helmets. The disadvantages of aromatic polycarbonates are its limited scratch and chemical resistance and a tendency to yellow with long-term ultraviolet exposure. As a consequence, for applications exposed to weathering or UV-radiation, specific surface treatments are needed. This can be either a coating (e.g. for improved abrasion resistance) or a coextrusion for enhanced weathering resistance.

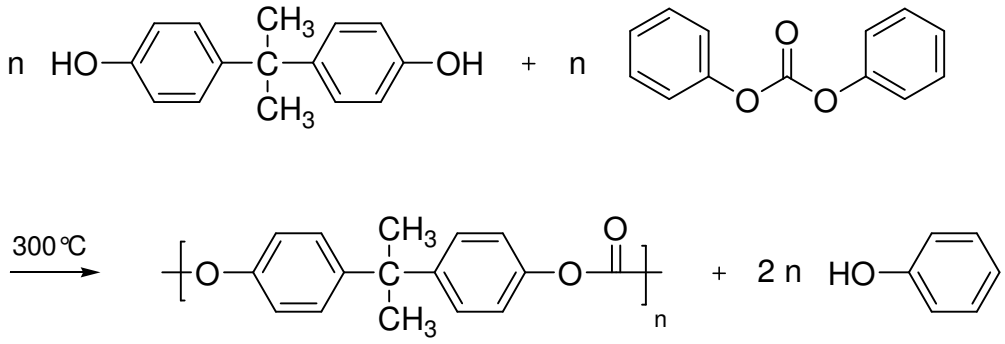
Aromatic polycarbonates can be synthesised by the polycondensation reaction from bisphenol-A and phosgene ($COCl_2$), as shown in Scheme 1.



Scheme 1 **Synthesis of poly(bisphenol-A carbonate) by the polycondensation of bisphenol-A and phosgene.[5]**

In this reaction, two molecules of hydrogen chloride (HCl) are formed for each repeating unit that is created. An improved way is to use the sodium salt of bisphenol-A in the polymerisation. Here, the formed by-product is sodium chloride (NaCl) instead of HCl. This is an obvious advantage because the salt will precipitate out of the organic solvent used in the polymerisation and therefore, can be removed easily and safely. Otherwise, the formation of the strongly acidic hydrogen chloride requires special advisements for the removal and in the selection of the construction material used in the polymerisation reactor.

There is a second industrial route for the synthesis of high molecular weight poly(bisphenol-A carbonate) (Scheme 2).

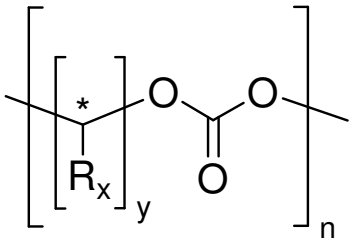


Scheme 2 **Synthesis of poly(bisphenol-A carbonate) by the transesterification of bisphenol-A and diphenyl carbonate.[6]**

This pathway consists of a melt phase transesterification between bisphenol-A and diphenyl carbonate. This reaction is environmentally more desirable than the one Scheme 1 shows, because here such unfavourable chemicals like phosgene and dichloromethane are not necessary. Additionally, the production of large amounts of NaCl as a side product is prevented. A disadvantage of the second route is that it requires high temperatures in order to remove phenol, the high boiling condensation product of this polymerisation reaction.

3.3 ALIPHATIC POLYCARBONATES

The class of aliphatic polycarbonates is as large as that of polyolefins. The alternating linkage of the carbonate groups with very variable alky sections opens a wide range of possibilities for chemists to synthesise polymers with specific material properties (Scheme 3). Due to their good biocompatibility, biodegradability and low toxicity, aliphatic polycarbonates are used as absorbable biomedical materials.[7,8]



Scheme 3 General structure of aliphatic polycarbonates.

By means of the alkyl block it is not only possible to vary the distance between two carbonate groups, but also to introduce various substituents and side groups with different nature and quantity into the polymer main chain. This incorporation creates stereo centres in the polymer and hence, makes accessible polycarbonates with different kinds of stereo regularity and material properties.

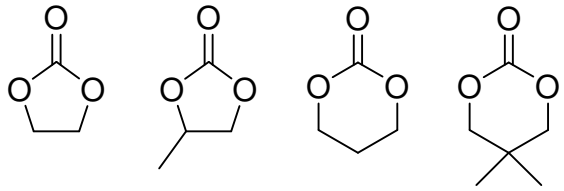
Aliphatic polycarbonates have potential applications in the synthesis of technical thermoplastics and resins, pyrotechnics and barrier layers for safety glass and of course as packaging materials.[9,10,11] The consistent and controllable decomposition of poly(propylene carbonate) (PPC) to cyclic propylene carbonate (cPC) below 250 °C, makes it predominantly useful as a binder for ceramics, adhesives and propellants.[12,13,14] The handicap for a broad utilisation of PPC as a bulk material is its low glass transition temperature (T_g) of 35-40 °C. Therefore, efforts are being directed to utilise aliphatic polycarbonates as additives and pore formers. One of the most promising applications is as mid-segment of polyurethanes.

The T_g of alicyclic polycarbonates, like poly(cyclohexene carbonate) (PCHC), is generally much higher (125°C), resulting in materials with attributes very similar to poly(styrene).[15] PCHC also has a higher decomposition temperature (about 300°C), which allows melt processing. Application areas of alicyclic polycarbonates are for example in lithographic processes for the construction of micro fluidic equipments.[16,17]

Attributes like low temperature of thermal deformation and moderate thermal stability hinder the widespread use of aliphatic polycarbonates as bulk polymeric materials as well as their high manufacturing costs (approximately 100 $ per pound).[18] The synthesis of improved new aliphatic polycarbonates and more economically feasible processes would obviously increase the number of their applications. The low activity of the currently industrial zinc/dicarboxylic acid catalysts, which are used to copolymerise CO_2 and epoxides, is one of the major contributors to the high costs of these materials.

3.4 RING-OPENING POLYMERISATION OF CYCLIC CARBONATES

The most commonly used cyclic carbonates for ring-opening polymerisation reactions (ROPs) are the 5-, 6- and 7-membered ring monomers. Among them, ethylene carbonate (EC), (cyclic) propylene carbonate (cPC), trimethylene carbonate (TMC) and 2,2-dimethyltrimethylene carbonate (DTC) have been investigated most systematically (Scheme 4). The ROP of these cyclic carbonates was achieved in the presence of alkaline, Lewis acids, enzymes and coordination catalysts, as described in the following chapters.

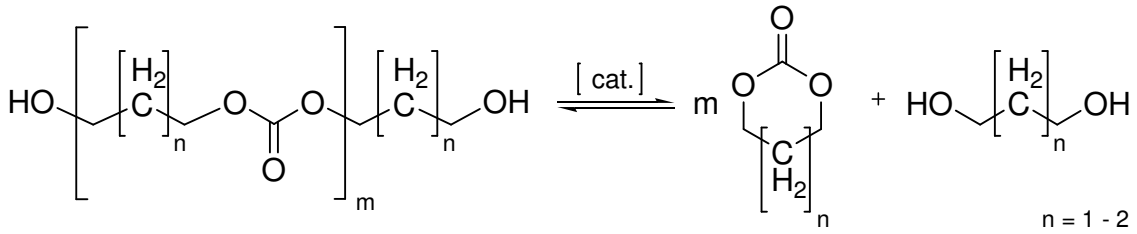


Scheme 4 Different cyclic aliphatic carbonates.

The ability of cyclic carbonate monomers to undergo ring-opening polymerisation depends on both thermodynamic and kinetic factors. The size of a ring and its strain as well as the kind and number of substituents determine the reaction enthalpy and entropy. Due to their relatively small ring strain, medium size rings (6- and 7-membered) have low enthalpies of ring-opening so that they can be polymerised with moderate exotherms.

3.4.1 SYNTHESIS OF ALIPHATIC CYCLIC CARBONATES

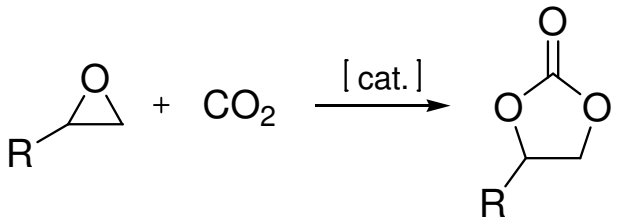
The synthesis of cyclic carbonates for the ring-opening polymerisation was first described by Carothers et al. in the early 1930s.[19,20,21] It was possible to isolate the cyclic carbonates through distillation after the depolymerisation reaction of linear polycarbonates at high temperatures in yields of 40-80% (Scheme 5).[22,23] The most effective catalysts in this process are the chlorides, carbonates or oxides of Sn(II), Mn(II), Fe(II) or Mg(II).



Scheme 5 Formation of 6- and 7-membered cyclic carbonates.

Nowadays, the process of depolymerisation of aliphatic oligocarbonates is still applied in the synthesis of 6-, 7-membered and even of larger size cyclic carbonates, i.e. cyclobis(alkylene carbonate)s. The process of depolymerisation of aliphatic polycarbonates is also utilised on a technical scale in ceramic technology and for nanofoam preparation.[24,25]

5-membered cyclic carbonates are easily available as a result of the insertion of carbon dioxide into an oxirane ring (mostly ethylene and propylene oxide) (Scheme 6).[26] The patent literature on the preparation of 5-membered cyclic carbonates is fairly extensive.[27,28,29,30,31,32,33,34]

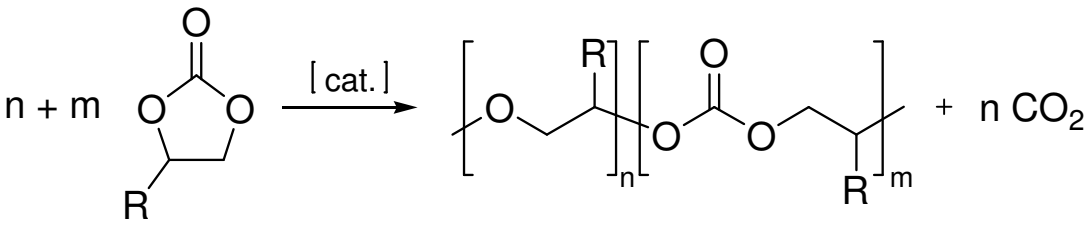


Scheme 6 Formation of 5-membered cyclic carbonates.

3.4.2 ROP OF 5-MEMBERED CYCLIC CARBONATES

Cyclic carbonates of the smallest ring size (5-membered) hardly undergo ring-opening. Their polymerisation, however, has been reported to proceed in the presence of metal alkoxides, metal acetylacetonates as well as metal alkyls as catalysts. It is characteristic that no polymerisation was found below 100°C for ethylene carbonate, but in the case of propylene carbonate the polymerisation does not take place significantly even at 140°C within a few days.[23,35] The reaction temperature of 170°C for EC and 180°C for cPC in the presence of

transesterification catalysts was found to be most suitable. The polymerisation involves partial decarboxylation. This loss of carbon dioxide during the polymerisation exceeds 50 mol% and is independent of the polymerisation conditions. Thus, the polymerisation of 5-membered ring alkylene carbonates fails to produce thermodynamically disfavoured poly(alkylene carbonate)s but leads to poly(alkylene ether carbonate)s with contents of carbonate units lower than 50 mol% (Scheme 7).



Scheme 7 ROP of 5-membered cyclic carbonates.

The reason for the high ether content is not the low ceiling temperature, but the positive enthalpy of the polymerisation.[36] Heitz et al. investigated a variety of catalysts for the polymerisation of ethylene carbonate, ranging from dibutyldimethoxytin to butyllithium, and found that the loss of CO_2 decreased as the alkalinity of the catalyst decreased.[37] Even under optimum conditions the maximum carbonate units in the copolymer of ethylene carbonate and ethylene oxide do not exceed 50%.

3.4.3 ROP OF 6-MEMBERED CYCLIC CARBONATES

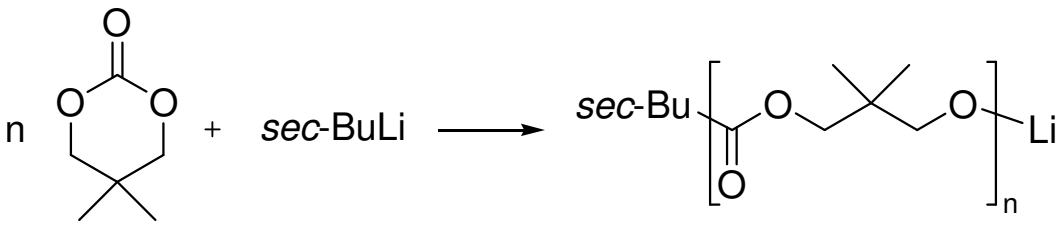
Contrary to the 5-membered cyclic carbonates, the 6-membered cyclic carbonates easily polymerise and copolymerise with various monomers. Carothers et al. were the first who reported about the homopolymer of a 6-membered cyclic carbonate in the early 1930s.[38,39] This homopolymer was obtained by heating 1,3-dioxan-2-one with a small amount of K_2CO_3. The molecular weight of the polycarbonates was rather low, not exceeding 4000 g/mol.

Pohoryles et al. discussed the stereochemistry and mechanism of the reversible polymerisation of 2,2-disubstituted trimethylene carbonates.[40] Thermal degradation of poly(trimethylene carbonate) leads to cyclic carbonate and carbonate oligomers as the main degradation products.[41]

It is characteristic that besides spiroorthocarbonates also some cyclic carbonates, as was found by Endo et al., exhibit an unusual attribute: their ring-opening polymerisation is accompanied by volume expansion.[42] The degree of volume expansion depends on the substituents and their position in the carbonate ring and ranges from 1.8 to 10.8%. For the polymerisation of trimethylene carbonate and 2,2-dimethyltrimethylene carbonate a volume expansion of about 3.5% was observed, while 1.8% for 2-*n*-butyltrimethylene carbonate.[43] The highest volume expansion (10.8%) of cyclic carbonate polymerisation was observed for 5-methyl-5-phenyl-1,3-dioxan-2-one anionic polymerisation.[44] The volume expansion was examined by assuming a change in molecular interaction between the monomer and polymer states.

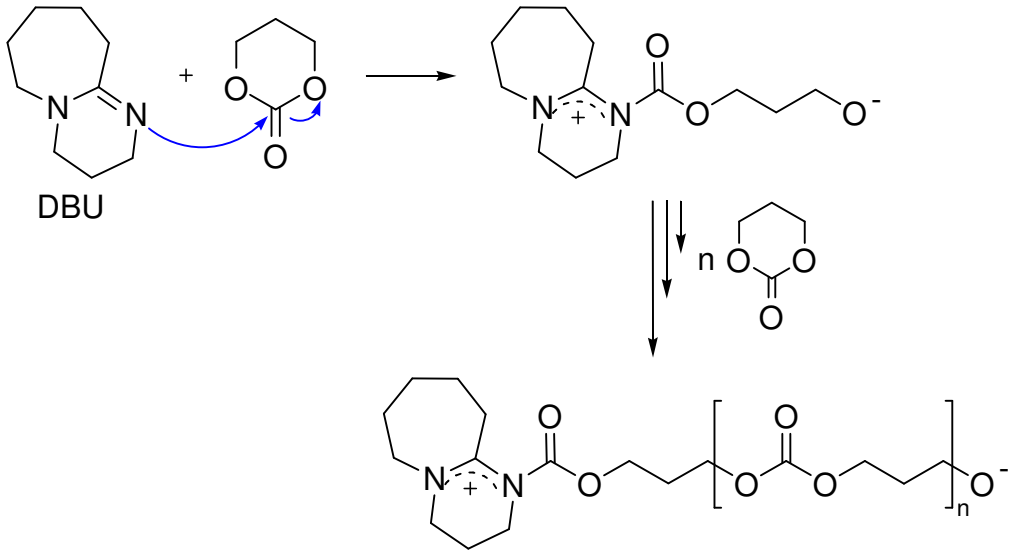
Anionic Polymerisation

In contrast to polycarbonates obtained with cationic initiators, high molecular weight polymers produced from 6-membered cyclic carbonates with anionic initiators do not contain ether units. This is especially important for oligocarbonates diols, which can be deployed as polyols for the polyurethane synthesis. Both, metal alcoholates and K_2CO_3 can be used as initiators. Other initiators based on alkali metals are *sec*-butyllithium (*sec*-BuLi) as well as sodium and potassium naphthalide (Scheme 8).[45]



Scheme 8 Anionic ring-opening polymerisation of DTC with *sec*-BuLi as initiator.

Endo et al. found that amine initiators such as 1,8-diazabicyclo[5,4,0]undecene-7 (DBU) could initiate the anionic ring-opening polymerisation of cyclic carbonates to afford the corresponding polycarbonate.[46] A plausible zwitterionic polymerisation mechanism (Scheme 9) was confirmed by FD-MS spectrum analysis of the polymerisation products, where besides cyclic oligomers a linear polymer with DBU end group was found. Thus, the initiating step of the polymerisation is the reaction between DBU and cyclic carbonate to form an alkoxide anion. In the propagation reaction the alkoxide anion attacks the carbonyl group of cyclic carbonate to yield the corresponding polycarbonate.

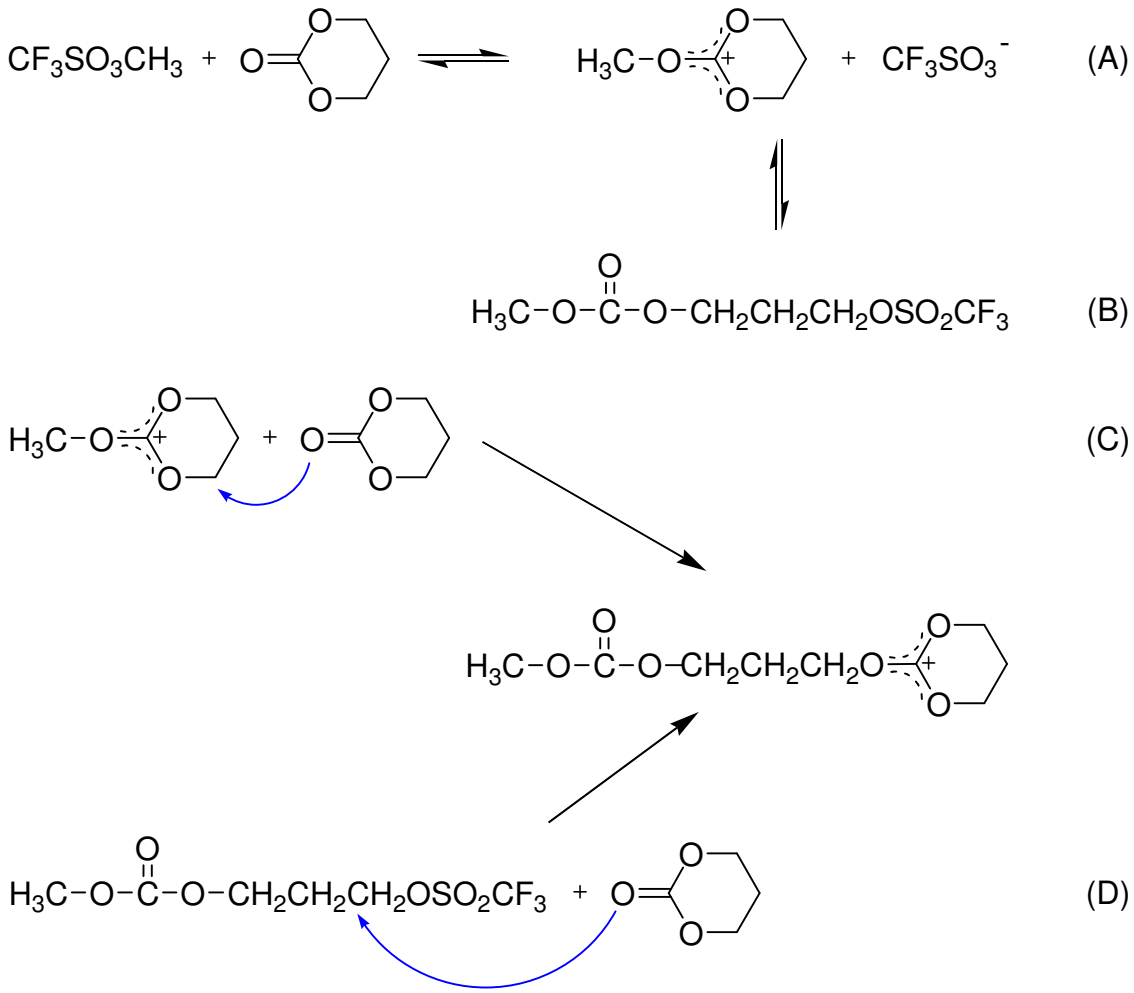


Scheme 9 Mechanism of the anionic ROP of TMC with DBU as initiator.

Cationic Polymerisation

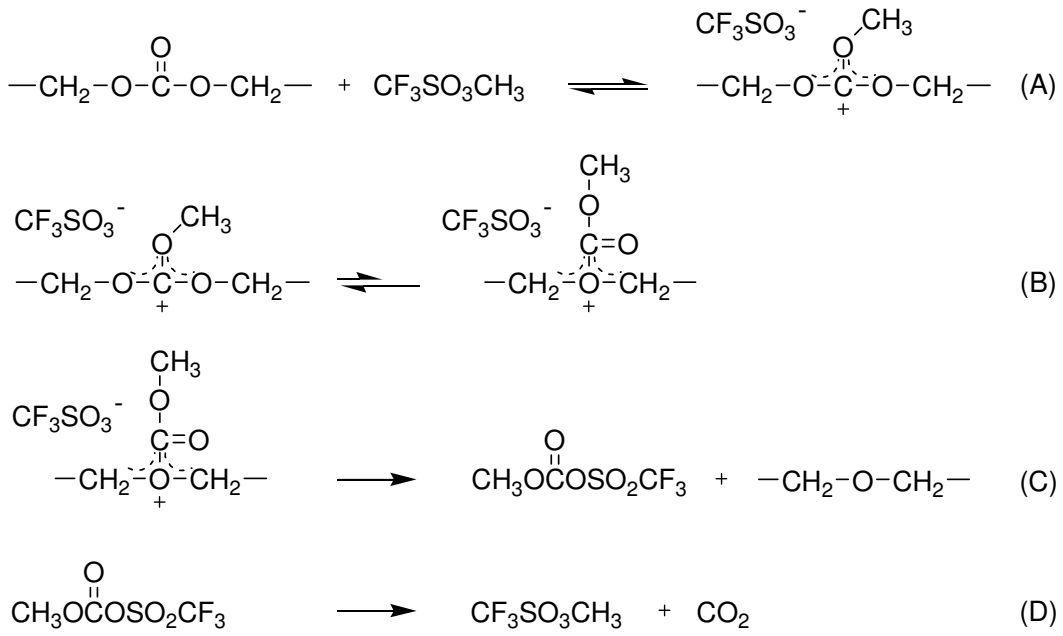
In the 1980s, Kricheldorf et al. introduced a suitable mechanism for the cationic ring-opening polymerisation of 6-membered cyclic carbonates (Scheme 10).[47] Using IR and ^{1}H NMR spectroscopy it was shown that methyl triflate initiates the polymerisation by alkylation of the *exo*-cyclic oxygen atom of the carbonate linkage, generating a trioxocarbenium ion **(A)**. The equilibrium with triflate is established after ring-opening by the counter-ion **(B)**. The first possible propagation step of the polymerisation is the attack of the trioxocarbenium ion on another monomer molecule leading to the alkyl-oxygen bond cleavage. The *exo*-cyclic oxygen atom of the nucleophile is alkylated **(C)**. The second possible

propagation reaction is the attack of the cyclic carbonate on the carbon atom next to the triflate end group **(D)**.



Scheme 10 Mechanism of the cationic ROP of TMC with methyl triflate as initiator.

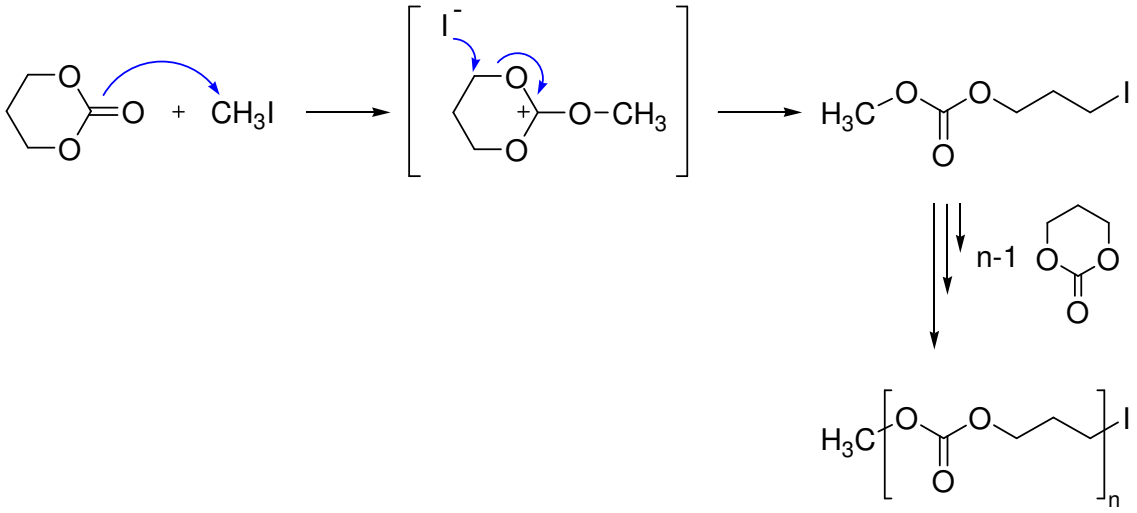
A possible side reaction of the cationic polymerisation of 6-membered cyclic carbonates is the decarboxylation reaction, which leads to the formation of ether groups. The mole concentration of the ether groups is in the range of 3-10% relative to carbonate groups and depends on the cationic initiator, the chemical structure of cyclic carbonate and the reaction temperature. The formation of ether linkages is explained by the intramolecular migration of an alkyl group. (Scheme 11).[47]



Scheme 11 Mechanism of the formation of ether linkages during the cationic ROP.

The equilibrium (B) is shifted to the trioxocarbenium ion due to its better stabilisation. But intramolecular migration is still possible and the initiator can be regenerated (D). The catalytic decarboxylation of carbonates was confirmed by the reaction of diethyl carbonate with 5 mol% of methyl triflate carried out under reflux. Slow CO_2 evolution and ether formation were observed. After 16 hours 30% conversion of carbonate linkages was found.[47]

Endo et al. have found that when alkyl halides were used as initiators for the cationic ROP of cyclic carbonates, the polymerisation proceeded without decarboxylation and the corresponding polycarbonates, although with rather low molecular weight, were formed exclusively.[48] The reactions of poly(trimethylene carbonate) with several cationic initiators including methyl iodide were monitored by ^{1}H NMR spectroscopy and gel permeation chromatography. Both, a decrease in the polymer molecular weight and an increase in the ratio of ether units strongly depend on the kind of initiator. The cationic polymerisations of different cyclic carbonates with a few alkyl halides such as methyl iodide (CH_3I), allyl iodide (CH_2=$CHCH_2I$) and benzyl bromide ($C_6H_5CH_2Br$) were carried out under various conditions and led to the corresponding polycarbonates without any ether units (Scheme 12).



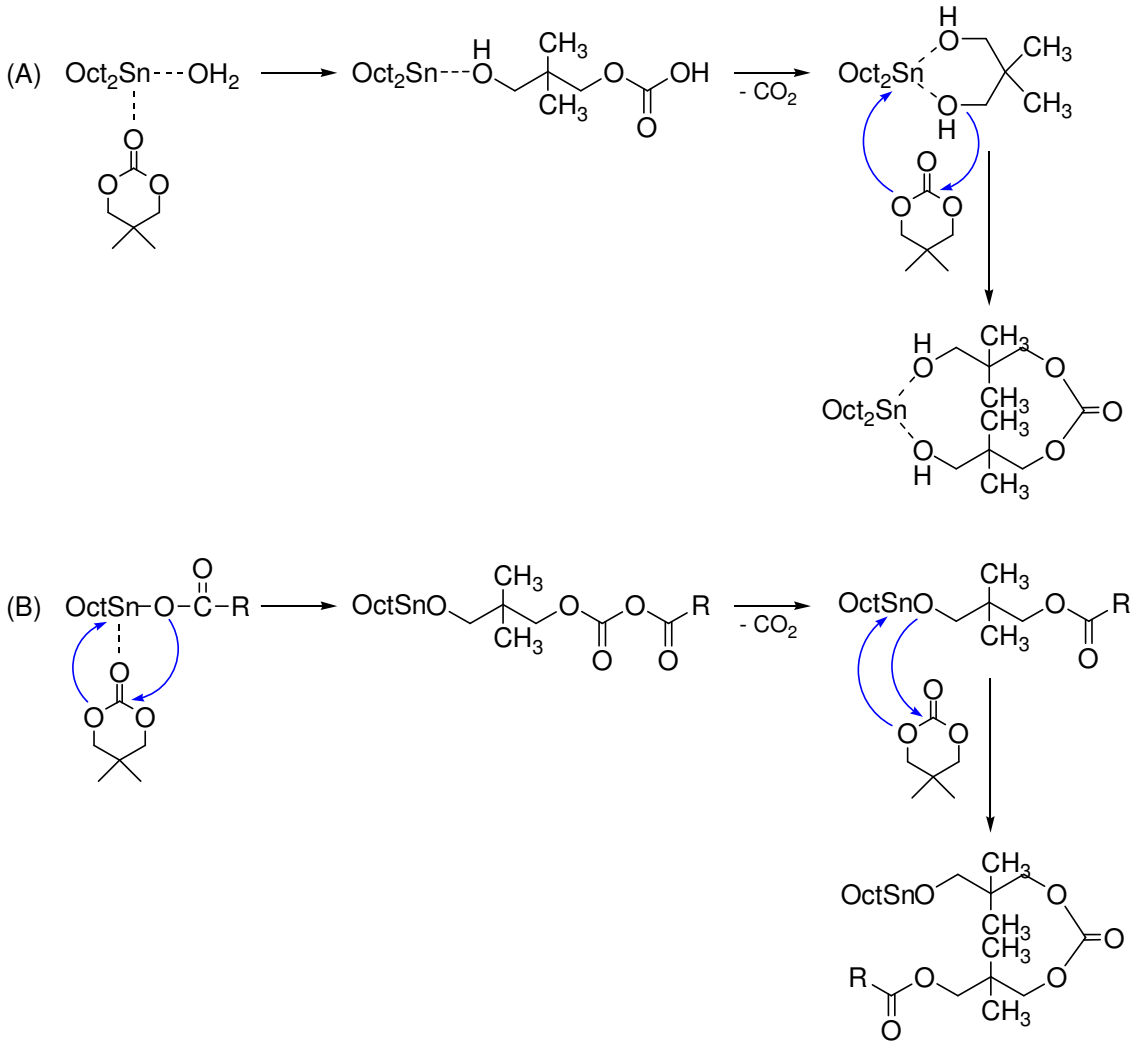
Scheme 12 Mechanism of the cationic ROP of TMC with methyl iodide as initiator.

Coordination Polymerisation

The coordination polymerisation of 6-membered cyclic carbonates carried out in the presence of metal carboxylates, e.g. zinc(II)stearate, of tin-based catalysts such as the di(*n*-butyl)stannic diiodide/triphenylphosphine system or of porphinatoaluminium compounds like (TTP)AlOR is not accompanied by the decarboxylation and yields respective polycarbonates.[49,50,51] The ring cleavage during the polymerisation of TMC and DTC in the presence of the above catalysts was found to occur at the C(O)-O bond, resulting in the formation of metal alcoholate propagating species.

Tin-2-ethylhexanoate ($SnOct_2$) is known to be a highly efficient initiator for the polymerisation of cyclic esters (lactides).[52,53] Moreover, Kricheldorf et al. found that $SnOct_2$ is also an efficient initiator for polymerisation of cyclic carbonates (Scheme 13). The molecular weights of $SnOct_2$-initiated polycarbonates correlate with the monomer/initiator ratio more or less. This finding and the ^1H NMR spectra suggest that stoichiometric reactions between monomer and $SnOct_2$ take place, yielding polymers with covalently bond 2-ethylhexanoate and OH end groups.

Two reaction pathways are proposed for ring-opening polymerisation of 6-membered cyclic carbonates with $SnOct_2$: **(A)** In the presence of small amounts of water or free 1,3-diols and **(B)** without such impurities (Scheme 13).



Scheme 13 **Mechanism of the coordination ROP of DTC with tin-2-ethylhexanoate.**

3.5 ALTERNATING COPOLYMERISATION OF CO_2 AND EPOXIDES

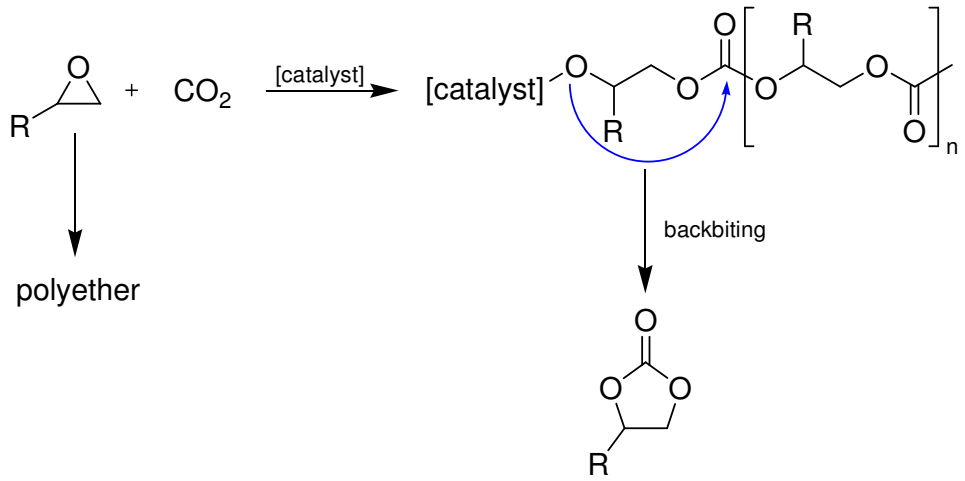
3.5.1 EARLY DISCOVERIES AND BACKGROUND

In 1969, Inoue et al. made the remarkable discovery that a mixture of diethyl zinc ($ZnEt_2$) and water was active for catalysing the alternating copolymerisation of carbon dioxide and propylene oxide (PO), marking the beginning of epoxide-CO_2 coupling chemistry.[54,55] An optimum 1:1 ratio of $ZnEt_2/H_2O$ gave the best yields of methanol-insoluble poly(propylene carbonate) (PPC) with an turn over frequency (TOF) of 0.12 (mol of PO converted to polymer per mol Zn per hour) at 80°C and 20-50 bar CO_2 pressure. On the basis of elemental analysis, the copolymer contained 88% carbonate linkages. Notably, a 1:1 mixture of $ZnEt_2$ and MeOH did not generate an active catalytic species for polycarbonate synthesis. Following this initial lead, Inoue investigated the use of dihydric sources, including primary amines, resorcinol and dicarboxylic acids, in mixtures with $ZnEt_2$ for the copolymerisation of CO_2 and PO.[56,57,58,59] These systems showed TOFs of 0.06, 0.17 and 0.43.

Following Inoue's discoveries, Kuran et al. developed a copolymerisation system using $ZnEt_2$ and trihydric phenols, including pyrogallol and 4-bromopyrogallol, that produced PPC with TOFs up to 0.3 at 35°C and 60 bar CO_2 pressure.[60,61] In general, di- or tri-protic sources and $ZnEt_2$ produced PPC, while mono-protic sources, such as alcohols and secondary amines, only gave cyclic propylene carbonate (cPC). In an effort to develop more active catalysts, Hattori et al. synthesised a heterogeneous catalyst from $Zn(OH)_2$ and glutaric acid. At 60°C and 30 bar CO_2 pressure, the $Zn(OH)_2$/glutaric acid mixture yielded PPC with a TOF of 1.1 and a molecular weight of 12.000 g/mol.[62]

3.5.2 GENERAL MECHANISTIC CONSIDERATIONS OF THE COPOLYMERISATION OF CO_2 AND EPOXIDES

The formation of aliphatic polycarbonates from epoxides and carbon dioxide, as shown in Scheme 14, can be achieved if an appropriate catalyst system is present.[63,64,65] The nature of the catalyst is key to the copolymerisation reaction. Several side reactions may occur which involve polyether or cyclic carbonate formation (Scheme 14). Ethylene oxide (EO) and 1-alkyl substituted epoxides are especially difficult to copolymerise because of the facile formation of cyclic products through a so-called backbiting reaction, a putative intramolecular reaction wherein a metal bond alkoxy chain end is presumed to attack the nearest carbonyl carbon in the chain. This behaviour was explained by the high mobility of the carbonate chain derived from such 1-alkyl-epoxides that would facilitate the formation of cyclic by-products. It is in marked contrast to, for example, the copolymerisation of cyclohexene oxide (CHO) and CO_2 that are much more easily transformed into the corresponding polycarbonate (poly(cyclohexene carbonate)). Cyclic propylene carbonate is a perfectly planar molecule but cyclic cyclohexene carbonate only exists in the *trans* isomer, which includes significant strain in the five-membered carbonate ring.[66,67] Darensbourg et al. suggested that this ring strain is most likely the major factor which leads to the favourable production of copolymer versus cyclic carbonate.



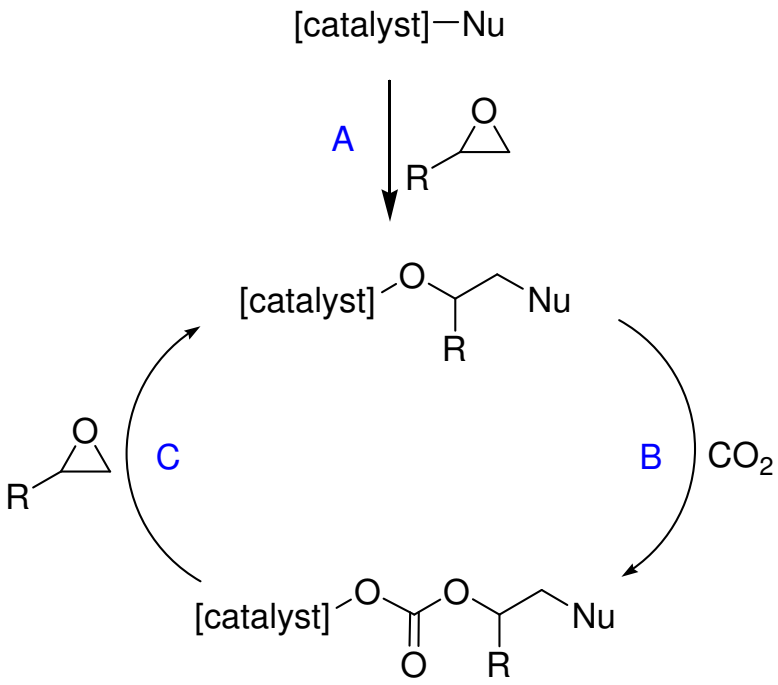
Scheme 14 **Copolymerisation reaction of 1-alkyl substituted epoxides and CO_2 with the formation of two possible by-products (polyether and cyclic carbonate).**

Some mechanistic insights into the copolymerisation with the various (heterogeneous) zinc catalysts were reported. An early study by Inoue on the copolymerisation of cyclohexene oxide and carbon dioxide shows the coordinated epoxide to be nucleophilically attacked from the backside, unusual and unexpected for single site catalysis with *syn* insertions at the metal centre as it is operative in olefin chemistry.[68] Another study by Inoue on a catalyst system prepared from polyhydridic phenols and diethyl zinc concludes after careful experimenting, that the active compound must encompass a Zn-alkyl entity (as Lewis acid) next to a zinc (di)phenoxide (as chain starter). Kuran et al. confirmed Inoue's experiments and in addition found substituent effects when applying functionalised phenols.[69,70] Related results were reported for example by Rätsch and Haubold for the $ZnEt_2/H_2O$ system.[71] They found that the most active system contains a zinc ethyl entity next to zinc oxy hydroxy species (the latter reacts with CO_2 to form the chain end). Both moieties need to be present for catalytic activity. The highest activity is obtained for a stoichiometry of $EtZn(OZn)_{2.2}ZnO_2COH$. Thus, the notion of a complex catalytic action, i.e. unlike single site catalysis, is definitely present in the early copolymerisation catalysis research.

In a more straightforward study on the copolymerisation of PO and CO_2 with aluminium porphyrines a direct bimolecular reaction mode of the ring-opening was proposed.[72,73] Also, Jacobsen reports several studies in which the derivatisation of epoxides is described with macrocyclic metal compounds in which several centres are working in concert.[74] Coates interpreted his results as well with zinc diketiminates as catalysts for the CHO/CO_2 and limonene oxide/CO_2 copolymerisation in terms of a multi site catalysis mechanism.[75,76] This is in contrast for example to earlier works of the group of Darensbourg on a catalyst system comprising chromium(III)-salen and an axial ligating compound, or to the work of Chisholm et al. on tetraphenylporphyrine aluminium complexes and to a quantum chemical study by Morokuma et al. on the copolymerisation of cyclohexene oxide and CO_2.[77,78,79] In later works, Darensbourg et al. found for the copolymerisation of cyclohexene oxide and CO_2 mediated by (*t*-butylacacen)chromium(III)-salen as catalyst, a mechanistically analogous

behaviour than we have shown earlier for the copolymerisation of propylene oxide and CO_2 mediated by chromium(III)-salophen catalysts.[80,81,82]

Obviously, the copolymerisation of epoxides and carbon dioxide is not a simple process. A formal general scheme for a copolymerisation system based on metal compounds can be formulated with the following elementary steps: **A)** Formation of a chain starting group through epoxide ring-opening. **B)** Preferred CO_2 insertion into a metal-alkoxide bond. **C)** Insertion of epoxide into a metal-carbonate bond (Scheme 15).



Scheme 15 **General reaction scheme for the copolymerisation of 1-alkyl substituted epoxides and carbon dioxide.**

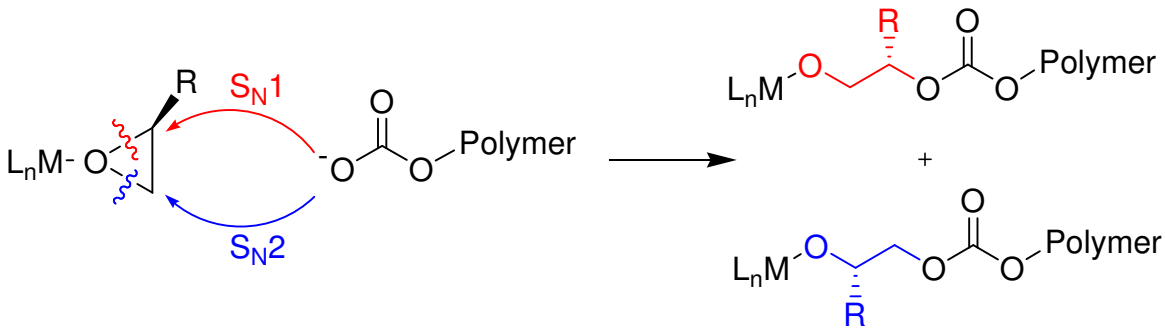
In this scheme, the metal centre of the catalyst acts as Lewis acid for the epoxide activation and, after ring-opening, enables the carbon dioxide insertion into its alkoxide bond. The alternating insertion of CO_2 and epoxide that is usually observed shows that the insertion of CO_2 into the metal-alkoxide bond and the consecutive reaction with an epoxide entity should at least be competitive.

The following paragraphs describe the two basic reaction steps in this alternating copolymerisation reaction and present possible mechanisms.

Epoxide Ring-Opening

Generally, epoxides can be polymerised by both anionic and cationic initiators due to the high degree of strain in the small 3-membered ring.[83]

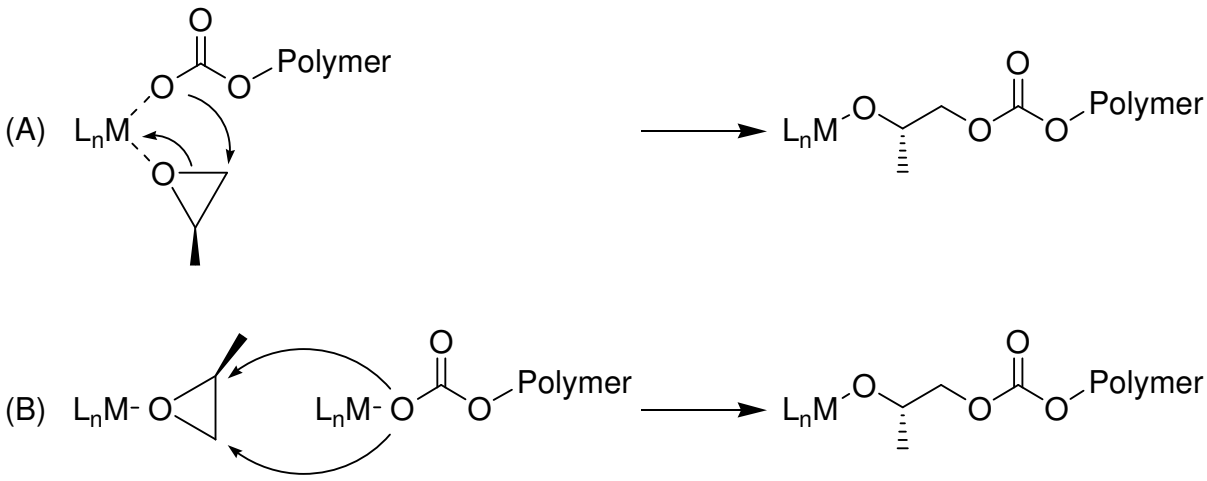
During the copolymerisation reaction of propylene oxide and carbon dioxide the ring-opening takes place via a nucleophilic attack of a carbonate species at one of the two ring carbons. The activation of the epoxide at the Lewis acidic metal centre makes this reaction easier because the ring carbons have a more electrophilic character and the carbon-oxygen bonds in the epoxide are weakened. In case of asymmetrical epoxides, such as propylene oxide, two ring-opening products are expected resulting from the attack at either the substituted or the non-substituted carbon atom (Scheme 16).



Scheme 16 **Epoxide ring-opening via nucleophilic attack of a free carbonate group (L_n = ligand system).**

The regiochemistry of this reaction depends strongly on the ring-opening mechanism. Lewis acid activated epoxides may be ring-opened via either S_N1 or S_N2 mechanism. The S_N1 mechanism favours tertiary carbon atoms and it could be expected that the attack of the carbonate group would be at the more substituted carbon and leads to retention of configuration. If the reaction follows S_N2 mechanism it could be expected that the attack takes place at the least hindered carbon atom and leads to inversion of stereochemistry of the substituted carbon.[84]

The mechanism of ring-opening in the epoxide/CO_2 copolymerisation reaction is still unknown so far. For a coordinate catalyst can be proposed two fundamental mechanisms as illustrated in Scheme 17 for propylene oxide.



Scheme 17 **Two fundamental mechanisms for the epoxide ring-opening: (A) migratory insertion and (B) backside attack.**

Pathway **(A)** shows a migratory insertion at a single metal site. This is similar to alkyl migration to a coordinated olefin or carbonyl ligand in organometallic chemistry.[85] The ring-opening may occur with inversion, retention or racemisation of stereochemistry. In pathway **(B)** the substrate and nucleophile are bound at different metal centres. The reaction proceeds via backside attack leading to inversion of stereochemistry (S_N2).

The second pathway seems to be the preferred mechanism so far. For the copolymerisation of cyclohexene oxide and CO_2, epoxide ring-opening was only observed under inversion of stereochemistry. This was independent of the applied catalyst and indicates a backside attack. Additionally, this is supported by speculations that two or more metal centres are involved in the CO_2/epoxide copolymerisation reactions.

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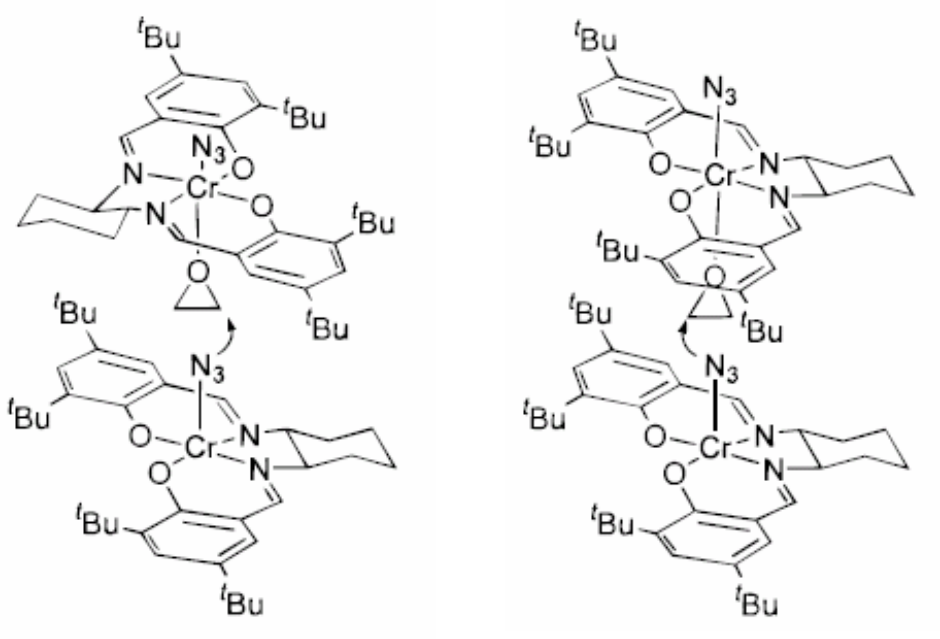
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CHAPTER 4

METAL-SALOPHEN CATALYSTS

4.1 INTRODUCTION

Jacobsen et al. found chiral chromium(III)-salen-chloride complexes to be highly active in the asymmetric ring-opening of epoxides.[1] Further studies led to a bimetallic mechanism in which one chromium complex acts as Lewis acid for epoxide binding and activation and another chromium complex as a delivery agent for the nucleophile (like chloride or azide) that ring-opens the epoxide (Scheme 1).[2]

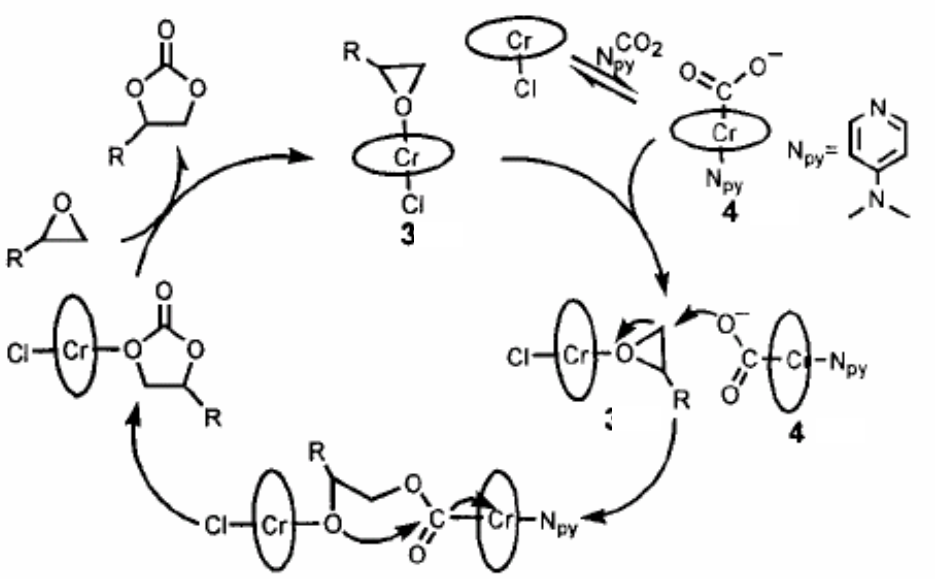


(A) head-to-tail (B) head-to-head

Scheme 1 Two possible transition states of the asymmetric ring-opening reaction of epoxides.

Scheme 1 shows two limiting geometries for the selectivity-determining step wherein the epoxide and azide are “sandwiched” between two complexes. **(A)** is a head-to-tail arrangement of the salen ligands wherein the diimine backbones are in a staggered conformation. **(B)** shows the head-to-head orientation of the salen ligands (eclipsed conformation), corresponding to a rotation of one of the salen units by 180°.

Paddock and Nguyen also reported about highly efficient chromium(III)-salen-chloride complexes for the synthesis of cyclic carbonates from terminal aliphatic epoxides (including propylene oxide, styrene oxide and epichlorohydrin) and CO_2 in 2001.[3] For their highly active catalytic system they needed to introduce a Lewis basic co-catalyst such as (4-dimethylamino)pyridine (DMAP) (Scheme 2). Paddock and Nguyen were the first to investigate the effect of catalyst/co-catalyst ratio on this coupling reaction. They found that the activity largely depends on DMAP concentration. Cyclisation activities increased when rising DMAP concentrations up to 2 equivalents but trailed off significantly at higher co-catalyst loadings. The reactions were carried out at approximately 3 bar CO_2 pressure and 75 – 85 °C with activities from 127 to 254 h^{-1}.



Scheme 2 Mechanistic proposal for the formation of cyclic carbonates via the DMAP-assisted chromium(III)-salen-chloride catalysis.

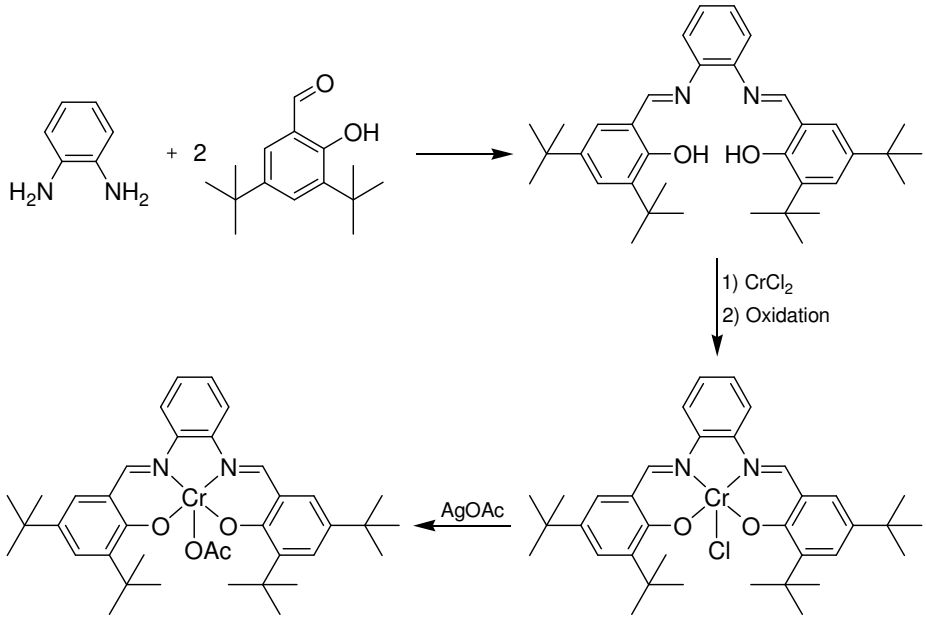
In deeper mechanistic investigations of this system our group could verify the strong dependence on the DMAP/chromium(III)-salophen ratio.[4] We showed that higher concentrations of DMAP assist the displacement of the growing chain from the chromium(III) centre and lead to an increased rate of chain degradation via backbiting the free alcoholate-terminated polymer chain.

4.2 EXPERIMENTAL PART

4.2.1 COMPLEX SYNTHESIS

4.2.1.1. SYNTHESIS OF THE CHROMIUM(III)-SALOPHEN-ACETATE COMPLEX

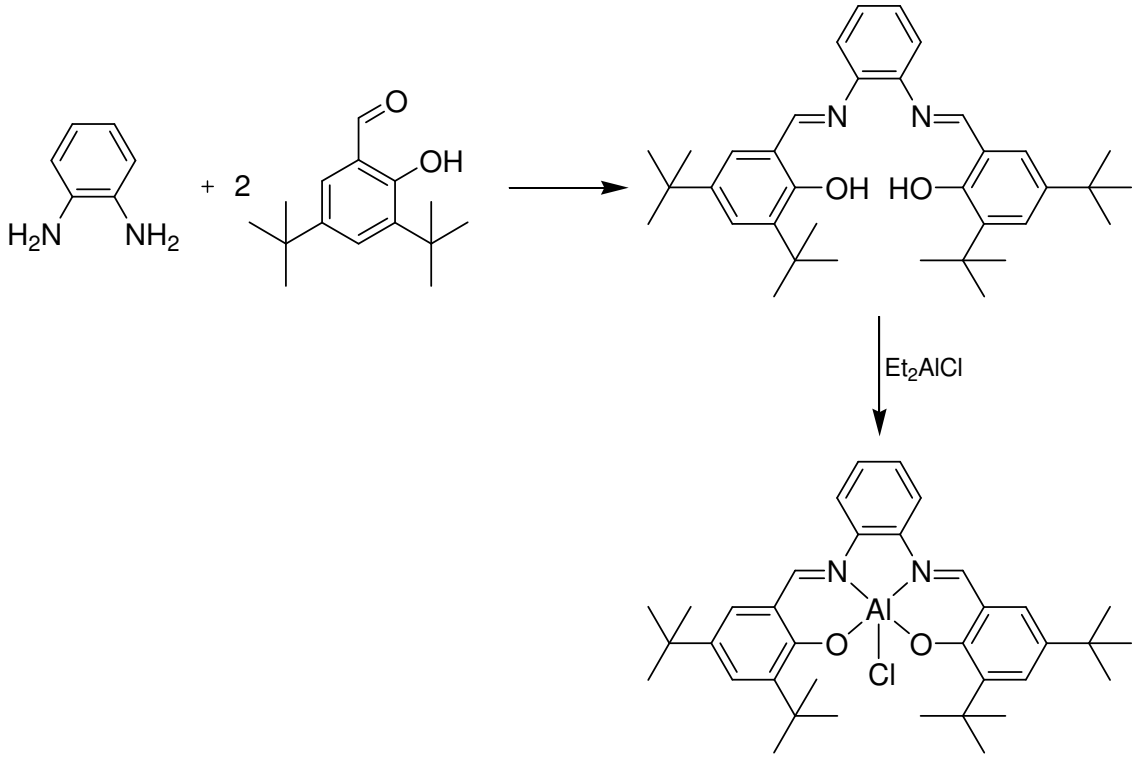
The salophen ligand was synthesised through a condensation reaction of 1,2-phenylenediamine and 3,5-di-*tert*-butyl-benzaldehyde in anhydrous ethanol. The complexation started with a solution of water free chromium(II) chloride ($CrCl_2$) and salophen ligand in anhydrous tetrahydrofuran (THF). The solution was stirred at room temperature under argon atmosphere for three hours. Afterwards, the flask was opened to air and the reaction mixture was stirred for additional three hours (oxidation from Cr(II) to Cr(III)). The product was washed with saturated solutions of sodium chloride (NaCl) and ammonium chloride (NH_4Cl). In order to obtain the chromium(III)-salophen-acetate complex a solution of chromium(III)-salophen-chloride and a slight excess of silver acetate in a mixture of THF and methylene chloride, was stirred for eight hours. Afterwards, the insoluble silver salts were filtered off (Scheme 3).



Scheme 3 **Synthetic pathway for the chromium(III)-salophen-acetate complex. The *tert*-butyl groups increase the solubility. The sixth coordination site of the chromium centre is occupied with a solvent molecule (e.g. THF), for clearer illustration this solvent molecule is omitted.**

4.2.1.2. SYNTHESIS OF THE ALUMINIUM(III)-SALOPHEN-CHLORIDE COMPLEX

The synthesis of the salophen ligand was analogue to the procedure described in chapter 4.2.1.1. For complexation, the ligand was dissolved in anhydrous toluene and a solution of diethyl aluminium chloride was added drop wise. The reaction mixture was stirred for 8 hours at room temperature (Scheme 4).



Scheme 4 **Synthetic pathway for the aluminium(III)-salophen-chloride complex. The *tert*-butyl groups increase the solubility. The sixth coordination site of the aluminium centre is occupied with a solvent molecule (e.g. toluene), for clearer illustration this solvent molecule is omitted.**

4.2.2 COPOLYMERISATION OF CARBON DIOXIDE AND PROPYLENE OXIDE

4.2.2.1. EXPERIMENTAL SETUP

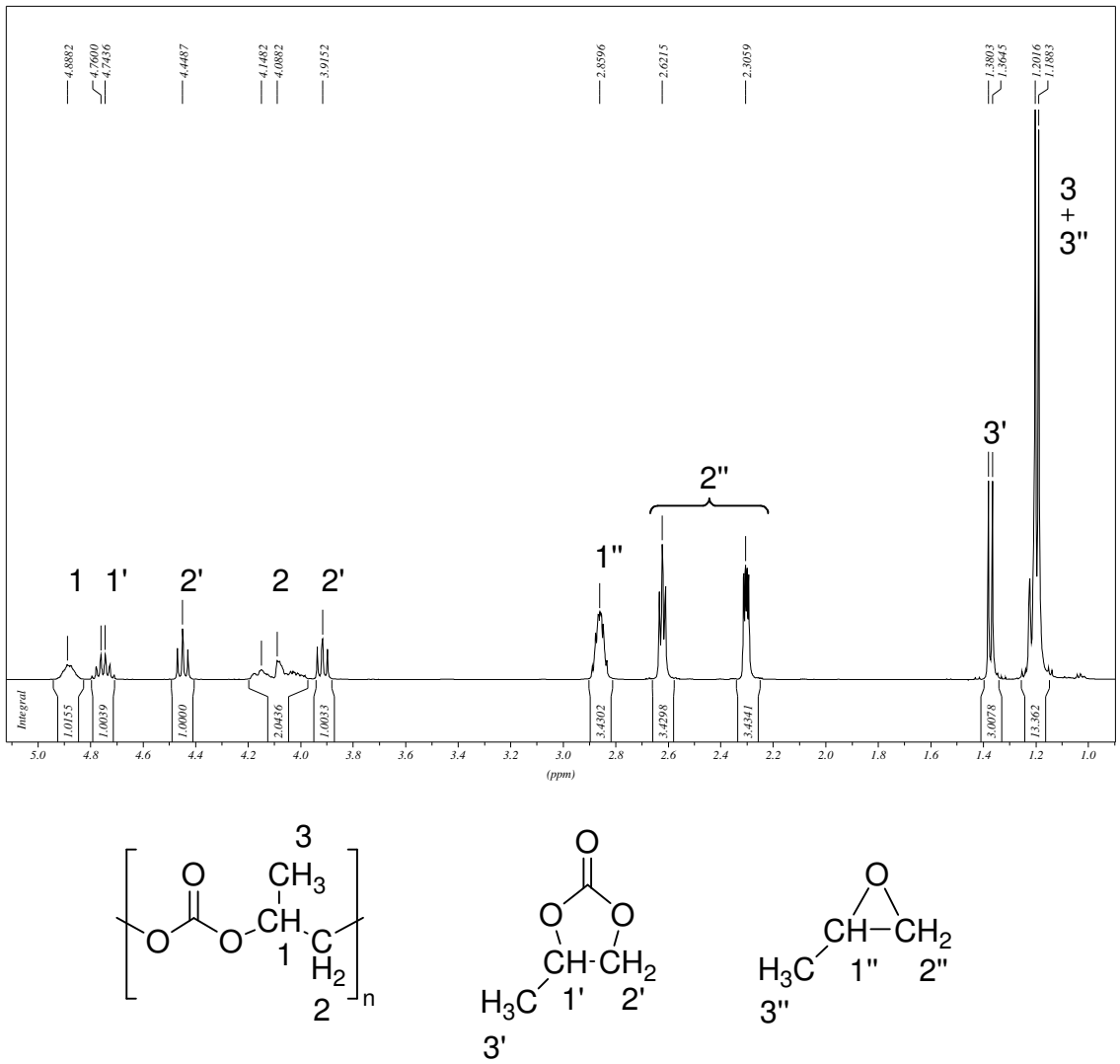
All polymerisation experiments were performed in 50 ml stainless steel Roth autoclaves equipped with oil bath heating and magnetic stirring (Figure 1). Prior to the reaction the autoclaves were dried at 80°C under vacuum. During the experiments the CO_2 pressure was kept constant by using a check valve. CO_2 of purity grade 4.5 was purchased from BASF Aktiengesellschaft Ludwigshafen and was applied in all reactions. In the present work, different catalysts and epoxides were employed which required individual polymerisation conditions.



Figure 1 **50 ml steel autoclave with CO_2 connection.**

4.2.2.2. CONDITIONS FOR CHROMIUM(III)-SALOPHEN AND ALUMINIUM(III)-SALOPHEN CATALYSED COPOLYMERISATION EXPERIMENTS

45.5 µMol of chromium complex, 45.5 µMol of aluminium complex and 0.5 to 2 equivalents of tetrabutyl ammonium chloride (NBu_4Cl) as co-catalyst were transferred into an autoclave followed by 1500 to 6000 equivalents of propylene oxide. The reaction vessel was closed and pressurised with CO_2 (4 to 25 bar). After heating the reactor for 10 minutes at 75°C, the destination pressure was adjusted (7 to 35 bar) and the reaction was allowed to run for 4 hours at 75°C. The autoclave was then cooled to 10°C and CO_2 was carefully vented off. Immediately after opening the autoclave a sample for ^1H NMR analysis was taken out of the crude reaction mixture to determine the product ratio (PPC/cPC) (Scheme 5). The viscous reaction mixture was diluted with CH_2Cl_2 and transferred to acidified (HCl) methanol resulting in precipitation of polycarbonate. The mixture was stirred for 2 hours. The isolated polycarbonate was dried under vacuum at 60°C. All resulting polycarbonates were analysed by ^1H NMR, ^{13}C NMR and GPC.



Scheme 5 **Attribution of the signals in the ^{1}H NMR spectrum of the crude polymerisation mixture.**

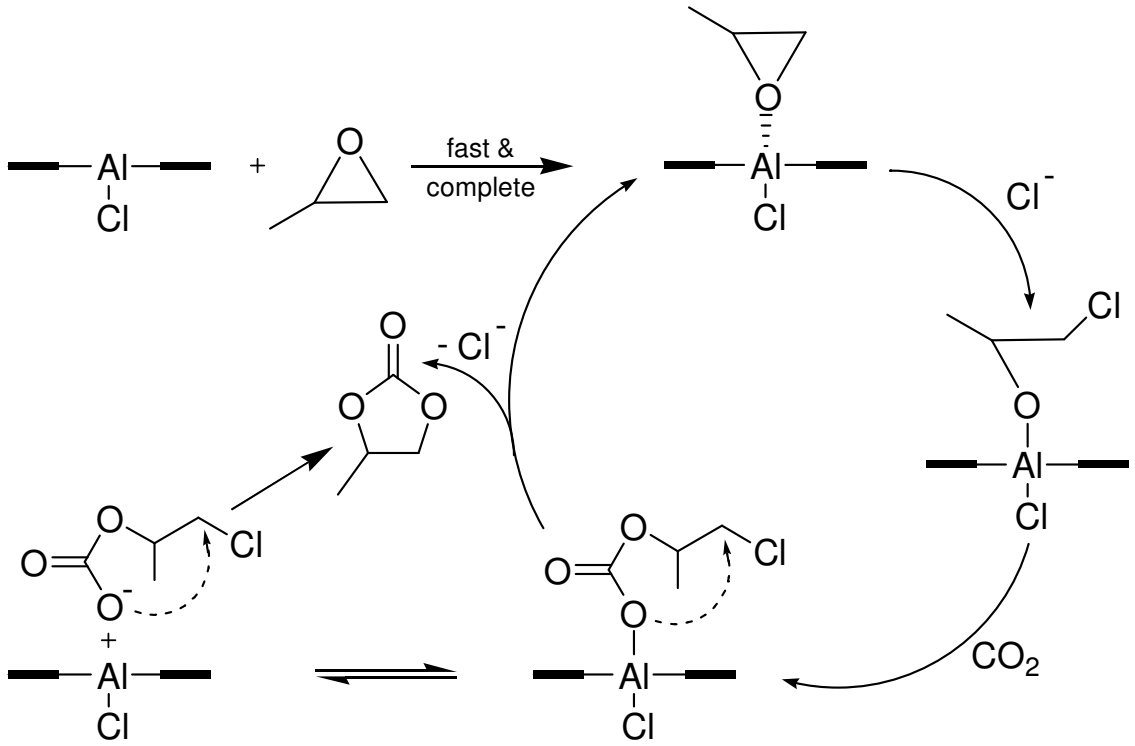
4.3 RESULTS

A first set of experiments aimed at the reactivity of aluminium(III)-salophen-chloride and epoxide/CO_2.[5] These experiments were carried out in a batch type process in neat propylene oxide (PO) over 4 hours and at 75°C. Results given are overall results for this reaction period. Formation of poly(propylene carbonate) (PPC) is not observed: cyclic propylene carbonate (cPC) is produced exclusively. PO conversion increases nearly linearly with the amount of activator (Table 1, entries 1-5). The catalysis becomes less than proportionally efficient with CO_2 concentration at higher pressure, which is indicative of a slow change in the rate-determining step. These observations are consistent with a reaction mechanism involving ring-opening through a fast external nucleophilic attack on a coordinated epoxide in a simple bimolecular process. The dependence on the CO_2 pressure is symptomatic for a slow insertion into the aluminium-alkoxide bond that eventually becomes competitive to nucleophilic attack at higher pressure. Decomposition of the carbonate species is apparently the fastest reaction in the system: chain propagation to yield PPC appears not to be competitive with the backbiting.

Entry	Metal-salophen complex	Co-catalyst	n(Nu) / n(metal)	% PO conversion	CO_2 [bar]	PO (equiv./cat.)	Equiv. PO in cPC
1	Al(III)-Cl	Cl^-	0.5	15	7	3000	450
2	Al(III)-Cl	Cl^-	0.5	30	14	3000	850
3	Al(III)-Cl	Cl^-	0.5	37	35	3000	1110
4	Al(III)-Cl	Cl^-	1	56	14	3000	1680
5	Al(III)-Cl	Cl^-	1	72[a]	35	3000	2196
6	Al(III)-Cl	^-OAc	1	2.5	7	3000	75
7	Al(III)-Cl	^-OAc	1	2.5	14	3000	75
8	Al(III)-Cl	^-OAc	1	3.3	25	3000	99
9	Al(III)-Cl	^-OAc	1	2.6	14	3000	78
10	Fe(III)-Cl	Cl^-	1	3	14	3000	90
11	Zn(II)	^-OAc	1	51	14	1500	765

Table 1 **Catalysis with salophen complexes of Al, Fe, Zn and a nucleophilic co-catalyst (chloride and acetate) at 75°C and 4 hours reaction time. Chloride was added as tetrabutyl ammonium, acetate as tetraethyl ammonium salt. [a] Extrapolated from a 2 hour experiment.**

DFT calculations performed by Dr. F. Molnar (BASF Aktiengesellschaft, Ludwigshafen) showed that the anion de-coordination reaction is particularly easy in aluminium(III)-salophen complexes. Even if small chains were formed, total decomposition of intermediate polycarbonate chains would be very efficient as soon as the carbonate anion is liberated from the complex (Scheme 6). Experiments with acetate as external nucleophile and with aluminium(III)-salophen-acetate as catalyst gave much lower conversions. The first nucleophilic attack is apparently slow. This is attributed to a less effective polarisation and, hence, activation of the epoxide (Table 1).



Scheme 6 **Formation of cyclic propylene carbonate with aluminium(III)-salophen-chloride and chloride as external nucleophile.**

Similar experiments were also performed for iron(III)-salophen-chloride and zinc(II)-salophen complexes. Here also the sole formation of cPC was found. However, the rates for iron(III)-salophen-chloride catalysed reactions were within one order of magnitude lower than that of aluminium(III)-salophen-chloride (Table 1, entry 10). The effective Lewis acidity of this complex is obviously lower than of aluminium or chromium and was not considered further in the studies. Zinc(II)-salophen complexes catalyse the copolymerisation of propylene oxide and CO_2 at a rate comparable to aluminium complexes.

A more complex situation is encountered in the chromium(III)-salophen/nucleophile catalytic system (Table 2). As reported before, the presence of a nucleophile is a basic prerequisite of the reaction.[6,7,8,9] In general both PPC and cPC are formed. The amount (concentration) of nucleophiles has a distinctive impact on the product distribution. Increasing the equivalents of co-catalyst relative to the salophen complex leads to the increased formation of cPC. At a ratio larger than one, cyclic propylene carbonate becomes the dominant product. This observation is independent of the type of nucleophile and also of the original counter ion in the chromium coordination sphere. There is, however, an influence on the rate of PO conversion and also on product ratios (Table 2, entries 1-6). The PPC formed generally has a carbonate linkage content of over 95%, however, at low concentrations of co-catalyst (nucleophile) ether linkages also occurred in the range up to 25%.

Entry	Catalyst	Co-cat.	cat./ co-cat.	%PO conv.	CO_2 [bar]	PO (equiv./cat.)	Equiv. PO in PPC	%PC in PPC	Equiv. PO in cPC	%PPC
1	Cr(III)-Cl	none	0	0	13	1500	-	-	-	-
2	Cr(III)-Cl[a]	DMAP	0.5	50	13	1500	615	91	135	82
3	Cr(III)-Cl	DMAP	1	68	13	1500	632	96	388	62
4	Cr(III)-Cl	DMAP	2	80	13	1500	-	-	1200	-
5	Cr(III)-Cl	Cl^-	1	56	13	1500	470	93	370	56
6	Cr(III)-Cl	^-OAc	1	29	13	1500	209	96	226	48
7	Cr(III)-OAc[b]	Cl^-	1	76	7	1500	490	91	650	43
8	Cr(III)-OAc	Cl^-	1	44	7	3000	1056	95	264	80
9	Cr(III)-OAc	Cl^-	1	23	7	6000	538	97	842	39
10	Cr(III)-OAc	Cl^-	1	77	14	1500	739	93	416	64
11	Cr(III)-OAc	Cl^-	1	52	14	3000	1310	95	250	84
12	Cr(III)-OAc	Cl^-	1	24	14	6000	1138	96	302	79
13	Cr(III)-OAc	Cl^-	1	68	35	1500	612	93	408	60
14	Cr(III)-OAc	Cl^-	1	30	35	3000	620	94	272	56
15	Cr(III)-OAc	Cl^-	1	18	35	6000	788	95	292	73
16	Cr(III)-OAc	Cl^-	2	46	14	3000	207	98	1173	15
17	Cr(III)-OAc	Cl^-	1	52	14	3000	1310	95	250	84
18	Cr(III)-OAc	Cl^-	0.5	52	14	3000	1388	91	153	89
19	Cr(III)-OAc	Cl^-	0.25	22	14	3000	261	76	405	39
20	Cr(III)-OAc	Cl^-	2	18	14	6000	414	99	405	51
21	Cr(III)-OAc	Cl^-	1	24	14	6000	1138	97	302	79
22	Cr(III)-OAc	Cl^-	0.5	46	14	6000	852	95	642	57
23	Cr(III)-OAc	Cl^-	0.25	22	35	3000	411	81	153	63
24	Cr(III)-OAc	Cl^-	0.5	46	35	3000	1071	91	165	78
25	Cr(III)-OAc	^-OAc	2	69	13	1500	300	99	735	29
26	Cr(III)-OAc	^-OAc	1	71	13	1500	586	96	479	55
27	Cr(III)-OAc	^-OAc	0.75	68	13	1500	592	95	428	58
28	Cr(III)-OAc	^-OAc	0.5	63	13	1500	595	92	350	63
29	Cr(III)-OAc	^-OAc	0.25	56	13	1500	622	89	218	74
30	Cr(III)-OAc	^-OAc	0	4	13	1500	-	-	60	-

Table 2 **Catalysis with chromium(III)-salophen complexes nucleophiles at 75°C and 4 hours reaction time. Chloride was added as tetrabutyl ammonium, acetate as tetraethyl ammonium salt. [a] 91 µmol. [b] 45.5 µmol.**

Both the concentrations of carbon dioxide and catalyst have also a marked impact on the PO conversion. Figure 2 illustrates the effects in case of chromium(III)-salophen-acetate complex using chloride (1 mol equivalent) as external nucleophile.

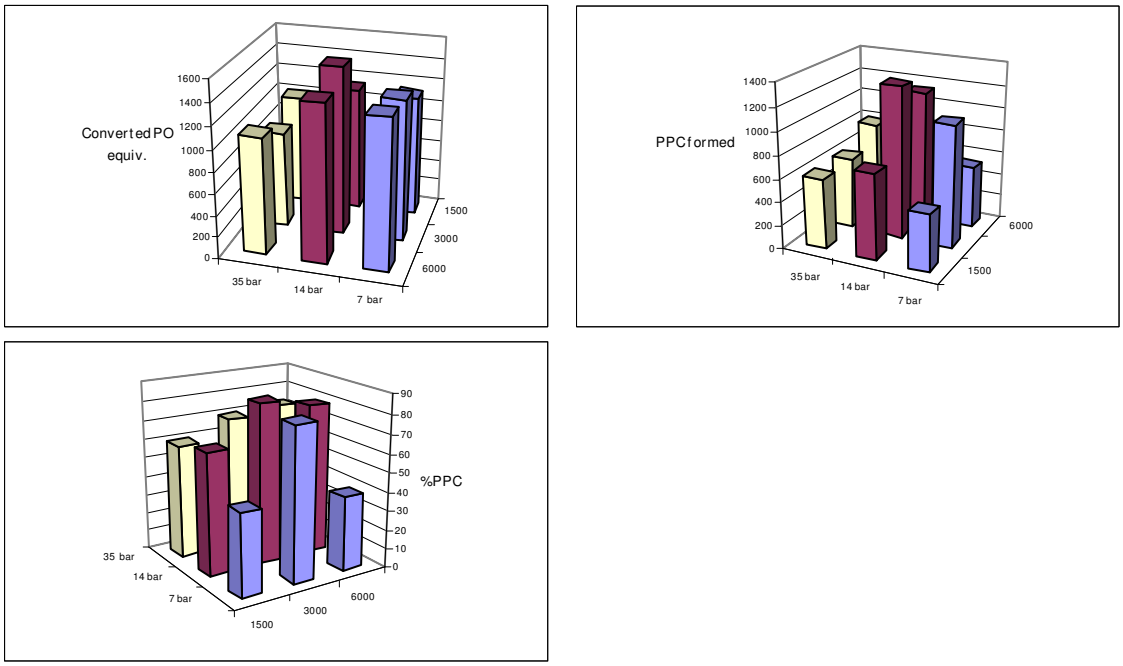


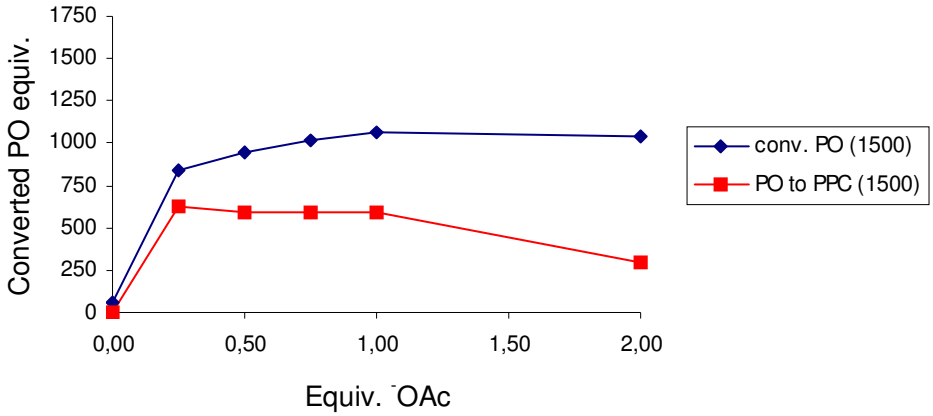
Figure 2 **Dependence of PO conversion, formed PPC and selectivity as function of CO_2 pressure and catalyst concentration (1500, 3000 and 6000 equivalents of PO) at 75°C using one mol equivalent of tetrabutyl ammonium chloride as co-catalyst.**

Regarding CO_2 pressure, it is easily figured out that higher pressures give lower rates. Also a higher concentration of catalyst (at 1500 mol equiv. of PO) leads to a lower absolute rate of PO conversion. The selectivity for polycarbonate formation is also complex, with favourable conditions at about 14 bar of CO_2 pressure and 3000 mol equivalents of PO per catalyst. The pressure dependence at that catalyst concentration is low. Using the combination of chromium(III)-salophen-chloride complex and acetate as nucleophile gives slightly different results with regard to selectivity and smaller conversion. This illustrates the importance of the starting conditions.

A study with various amounts of acetate as nucleophile and chromium(III)-salophen-acetate complex as catalyst shows the effect of the external

nucleophile concentration (Figure 3 **(A)**). The yield of PPC slowly decreases up to a ratio of acetate to chromium(III) of 1 to 1 with a continuously growing part of PO being transformed into cPC. Beyond this ratio the polymer yield decreases rapidly at constant rate of PO consumption. When using a system of chromium(III)-salophen-chloride and chloride as external nucleophile the behaviour is similar, but now a clear maximum for activity and selectivity is observed. The best ratio for PPC formation at 3000 equivalents PO per chromium(III) was about 0.5, respectively 1 at 6000 equivalents. It is noticeable that the optimum conditions for polycarbonate formation are a function of the catalyst concentration: at higher dilution the conversion of PO decreases as well as the selectivity for PPC.

(A)



(B)

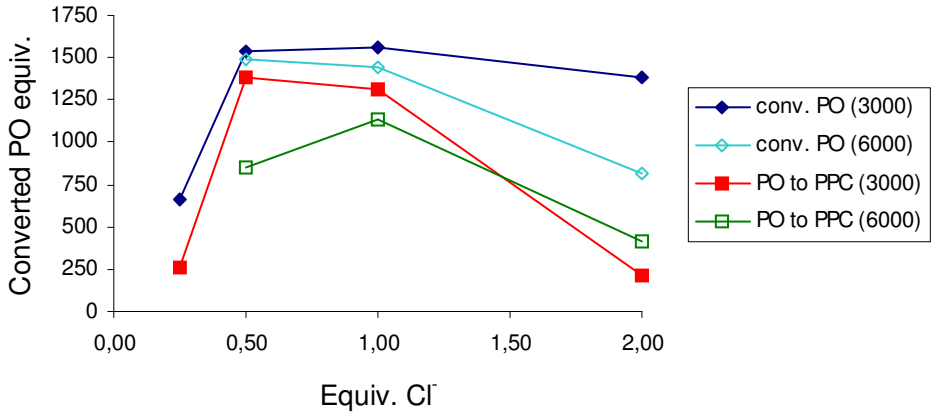


Figure 3 **(A) Conversion of PO (1500 equiv.) and formation of PPC using chromium(III)-salophen-acetate complex and tetraethyl ammonium acetate at 75°C (13 bar of CO_2 pressure and 4 h of reaction time). (B) Using chromium(III)-salophen-chloride and tetrabutyl ammonium chloride at 75°C (14 bar of CO_2 pressure).**

This system of chromium(III)-salophen-chloride/chloride was studied in more detail at 65°C, at which rates are lower (Table 3).

Entry	CO_2 [bar]	% PO conversion	Equiv. PO in PPC	Equiv. PO in cPC	% PPC	Time [h]
1	2	23	48	642	7	3
2	5	17	122	388	24	3
3	10	23	186	504	27	3
4	12.5	22	132	528	20	3
5	16	13	148	246	38	3
6	16	13	179	211	46	3
7	16	14	176	244	42	3
8	18	11	175	155	53	3
9	21	9	108	162	40	3
10	16	14	126	294	30	1.5
11	16	8	98	142	41	6
12	16	10	502	428	54	10
13	16	20	719	691	51	20

Table 3 **PO conversion (3000 equivalents) at 65°C mediated by chromium(III)-salophen-chloride and tetrabutyl ammonium chloride as function of CO_2 pressure and reaction time. The triplicate results (entries 5-7) illustrate the limited reproducibility.**

Figure 4 **(A)** shows the dependence of the PO conversion (3000 equivalents of PO and 0.5 equivalents of chloride) and selectivity for PPC at 16 bar CO_2 pressure as function of the reaction time. The dependence of the CO_2 pressure at 3 hours reaction time is shown for the same system in Figure 4 **(B)**. The catalysis obviously has an induction period in which the selectivity is low for PPC formation. With reaction time progressing, however, PPC becomes the major product. Again, the conversion of PO is lower at higher CO_2 pressure. The catalytic action is independent of the concentration of cPC. An experiment with 10% cPC dissolved in PO gave the same overall conversion and selectivity. Thus quite a complex behaviour is found, again inconsistent with a scheme involving only consecutive reactions at a single catalyst site.

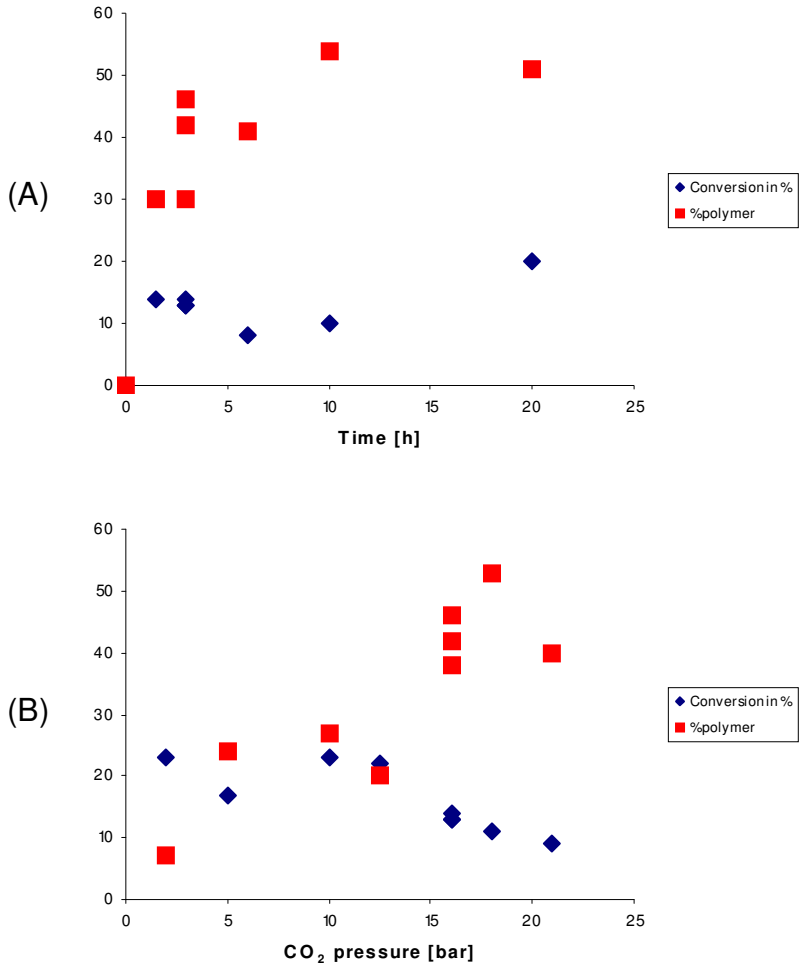


Figure 4 **(A) PO conversion and selectivity at 65°C and CO_2 pressure of 16 bar as function of time. (B) PO conversion and selectivity with 0.5 mol equivalents of tetrabutyl ammonium chloride as co-catalyst and 3 hours of reaction time as function of CO_2 pressure.**

Without detailed mechanistic and kinetic studies and starting from several feasible intermediates, a well proven description of the chromium-salophen system cannot be given. However, taking the essentials of the aluminium(III)-salophen catalysis, the action of chromium system can be understood if extended with intermolecular chain growth and including anion dissociation as the rate-determining step for cPC formation. The following argumentation supports and illustrates this hypothesis.

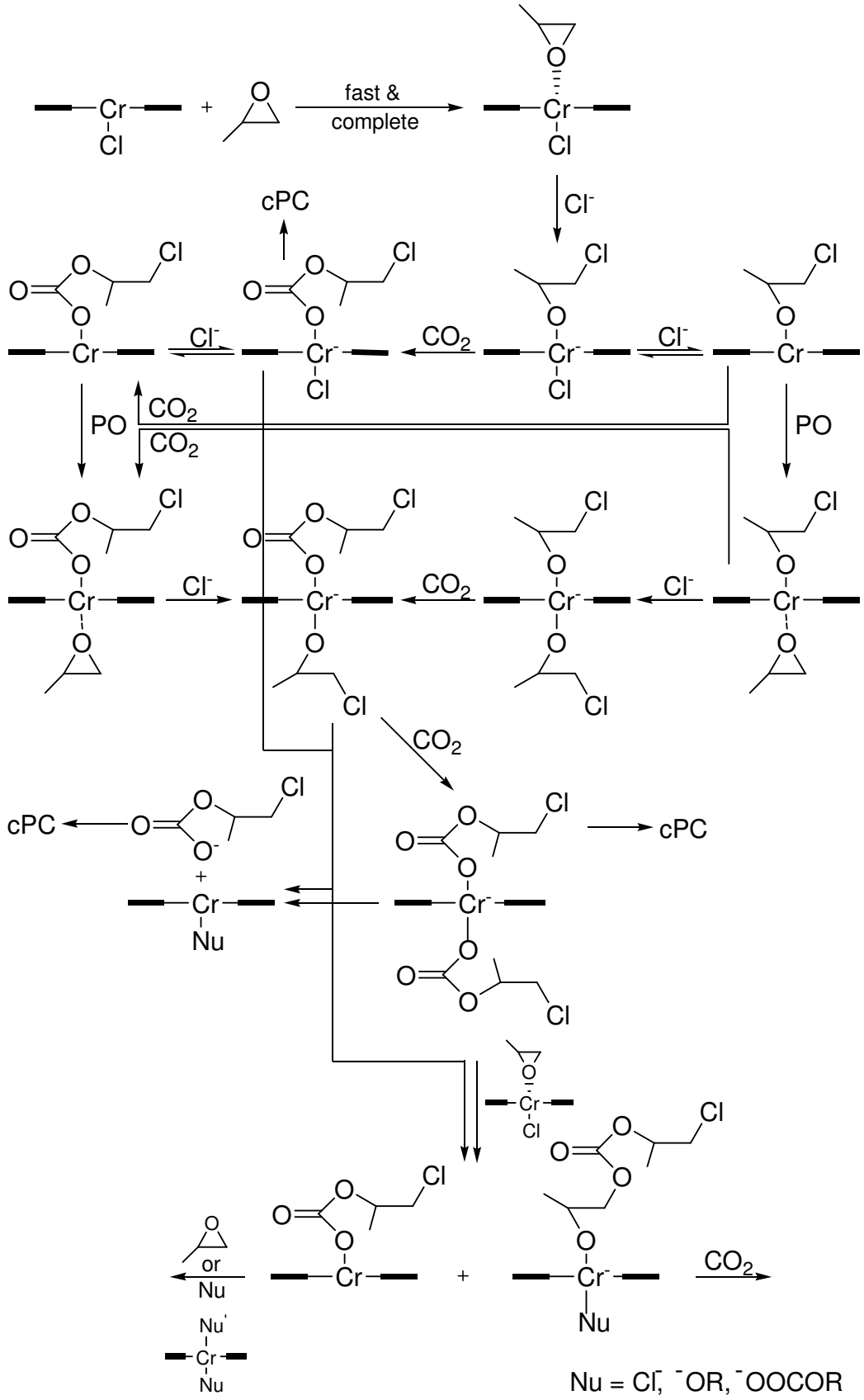
The presence of a (more than) stoichiometric amount of nucleophiles in the catalysis leads to complete conversion of the chromium starting complex to a 6-coordinate species and implies that only few coordination sites in the salophen complex will be free: the concentration of coordinated (activated) epoxide is relatively low and any bimolecular chain formation is therefore slow. Thus, the resulting activity is similar to that of aluminium(III)-salophen-chloride within the aluminium(III)-salophen-carbonate species simply decompose to cPC. Anion dissociation is more extensive at higher dilution, thus, better conversions are reached at 3000 than at 1500 equivalents of PO, as more epoxide is activated. Further dilution gives a slightly lower PO conversion, possibly caused by a less effective bimolecular reaction between nucleophile and coordinated epoxide resulting in a less effective chain growth. A bimolecular reaction is understood here as either attack by a free carbonate group, formed through anion dissociation, or by a metal bound nucleophile. The selectivity for PPC formation, (as shown in Figure 2) has a maximum at 3000 equivalents of PO. This can be explained by the increasing concentration of activated epoxide at higher extend of anion dissociation and a lower effectiveness at increasing dilution of bimolecular reaction with the concomitant decrease at 6000 equivalents of PO.

At higher CO_2 pressure both a lower rate of PO conversion and a higher yield of polycarbonate are observed (Figure 2 and Table 3). This behaviour can be explained by taking the nucleophilicity of 5- and 6-coordinate chromium(III)-salophen-carbonate complexes into consideration. These species are expected to coordinate in the *trans* position at longer reaction times and at higher pressure. So all nucleophiles that have been present at the beginning, including those in the coordination sphere of chromium, get the possibility to react with PO and eventually become bis-carbonate complexes. Epoxide activation is less effective in complexes with a coordinated carbonate in the *trans* position, resulting in lower conversion rates at higher pressures and longer reaction times. In addition, anion dissociation is more endothermic for alkoxide-carbonate or chloride-carbonate than for a carbonate-carbonate salophen complex. Cyclic carbonate formation is thus more effective in the early phase of the catalysis or at low pressures when strong nucleophilic *trans* ligands induce the liberation of the carbonate entities. Consistently, Figure 4 shows this dependence as well as

the expected limited reproducibility at short reaction times. The catalysis thus is also expected to proceed through an initiation phase to reach a steady state as observed by Darensbourg et al.[10] Ether linkages in the polycarbonate chain are particular prominent at high catalyst concentrations and low ratios of nucleophiles. In those cases, the concentration of coordinated epoxides is relatively high, nucleophilic attack of a chromium(III)-salophen-alkoxide species becomes competitive to CO_2 insertion and polyether is formed.

Scheme 7 pertains the catalysis with chromium(III)-salophen compounds as discussed above, without taking all anion exchange processes explicitly into account that certainly occur. The first presumption is the fast and complete formation of epoxide-coordinated complexes that are nucleophilically attacked by the co-catalyst, resulting in negative charged 6-coordinated alkoxide complexes. This first anionic compound in the catalytic cycle may insert CO_2 resulting in a carbonate complex. In addition the exchange of anionic entities is expected to proceed among all chromium species, i.e. the chloride atom de-coordinates from the 6-coordinated alkoxide/chloride complex either in a spontaneous process or through reaction with any 5-coordinated chromium(III)-salophen complexes. The 6-coordinated carbonate complex also could also be the result of an anion abstraction, CO_2 insertion and anion coordination reaction sequence. Scheme 7 is thus a simplified picture of some of the feasible reactions in the system. It demonstrates the most prominent pathways in the catalytic cycle.

In contrast to the aluminium(III) based conversion of PO and CO_2, anion dissociation is presumed to be much slower and thus, has become the rate-determining step for the formation of cPC. The resting state is accordingly the carbonate complex.



Scheme 7 **Copolymerisation scheme of PO and CO_2 mediated by chromium(III)-salophen-chloride complexes and chloride as co-catalyst.**

The given details and data show that a multistep and multicentre catalysis is a feasible and perhaps likely option: it makes the experimental observations explainable. However, the only circumstantial evidences found for multisite chemistry is the parabolic plot for PPC formation and PO conversion and furthermore the polyether microstructures found at high catalyst concentration in combination with low ratios of nucleophiles and low CO_2 pressures.

In order to investigate the importance of two metal centres reacting together for the formation of PPC, experiments were performed with mixtures of aluminium(III)- and chromium(III)-salophen complexes. The catalytic system based on two different salophen complexes offers the possibility to analyse the interaction between the active centres if the individual components differ substantially in their characteristic catalytic actions. The chromium(III)-salophen-acetate and aluminium(III)-salophen-acetate/chloride complexes fulfil this requirement. The results are shown in Table 4.

Entry	$n(Cr^{III})$ [µmol]	$n(Al^{III})$ [µmol]	$n(Nu^-)$ / $n(Cr^{III})$	CO_2 [bar]	PO (equiv./Cr^{III})	total PO conversion	Equiv. PO in PPC	Equiv. PO in cPC	% carb. linkage	T [°C]
	Cr-OAc	**Al-OAc**	**$^-$OAc**							
1	45,5	0	1	14	3000	617	495	120	100	65
2	0	45,5	1	14	3000	120	0	78	0	65
3	45,5	45,5	1	14	3000	573	474	99	100	65
4	45,5	0	1	14	3000	1342	1026	300	99	75
5	0	45,5	1	14	3000	75	0	75	0	75
6	45,5	45,5	1	14	3000	1833	1413	336	95	75
7	45,5	0	1	35	3000	888	735	153	100	75
8	0	45,5	1	35	3000	99	0	99	0	75
9	45,5	45,5	1	35	3000	1311	996	276	97	75
	Cr-OAc	**Al-Cl**	**Cl^-**							
10	45,5	0	1	35	3000	582	381	201	100	75/2
11	45,5	45,5	1	35	3000	714	326	389	100	75/2
12	45,5	136,5	1	35	3000	848	323	525	100	75/2

Table 4 **Experiments with chromium(III)-salophen-acetate, aluminium(III)-salophen-acetate or -chloride and either acetate or chloride as external nucleophiles.**

Entries 1-9 in Table 4 relate to experiments performed with chromium(III)-salophen-acetate and aluminium(III)-salophen-acetate complexes with acetate as co-catalyst. Experiments were prepared at 65°C or 75°C. It was found, that the resulting product mixtures are basically determined by the catalytic action of the chromium(III)-salophen complex, with slightly higher ether contents in the resulting polycarbonates. This might not be surprising, since the catalytic activity of aluminium(III)-salophen-acetate complexes in the PO/CO_2 conversion is not particularly high.

Effects should show up, if at all, most significantly in the early phase of the copolymerisation reaction and at higher concentration of CO_2. To investigate this behaviour a further set of experiments was performed at 75°C, 35 bar CO_2 pressure and 2 hours of reaction time applying the aluminium(III)-salophen-chloride complex instead of the aluminium(III)-salophen-acetate complex (Table 4, entries 10-12). Now the product constitution shows a change. The formation of PPC is in first approximation independent of the amount of aluminium(III)-salophen complex, however, the ratio of PO converted to cPC is strongly increased. This could have various reasons. On the one hand, nucleophiles may have reacted with epoxide coordinated to aluminium with consecutive formation of cPC. A simple analysis shows that this is not the case: an experiment with a threefold excess of aluminium(III)-salophen-chloride over chromium(III)-salophen-acetate shows that a minimum of about 30% of the nucleophiles were associated with aluminium(III) to account for the cPC formed. The remaining 70% on chromium(III), however, should have resulted in much more PPC as is known from the behaviour of chromium(III)-salophen-acetate (Figure 3, **(B)**). Since this is not observed, processes involving interactions between both species must be considered.

One possibility is that chain ends are transferred from chromium(III) to aluminium(III), leading to decomposition of the polycarbonate chain. Though, aluminium(III)-salophen related cPC formation should be linear dependent on its concentration. Figure 5 shows this nearly linear dependency.

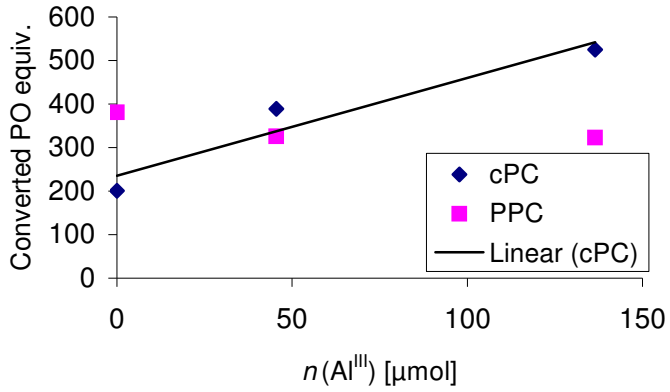
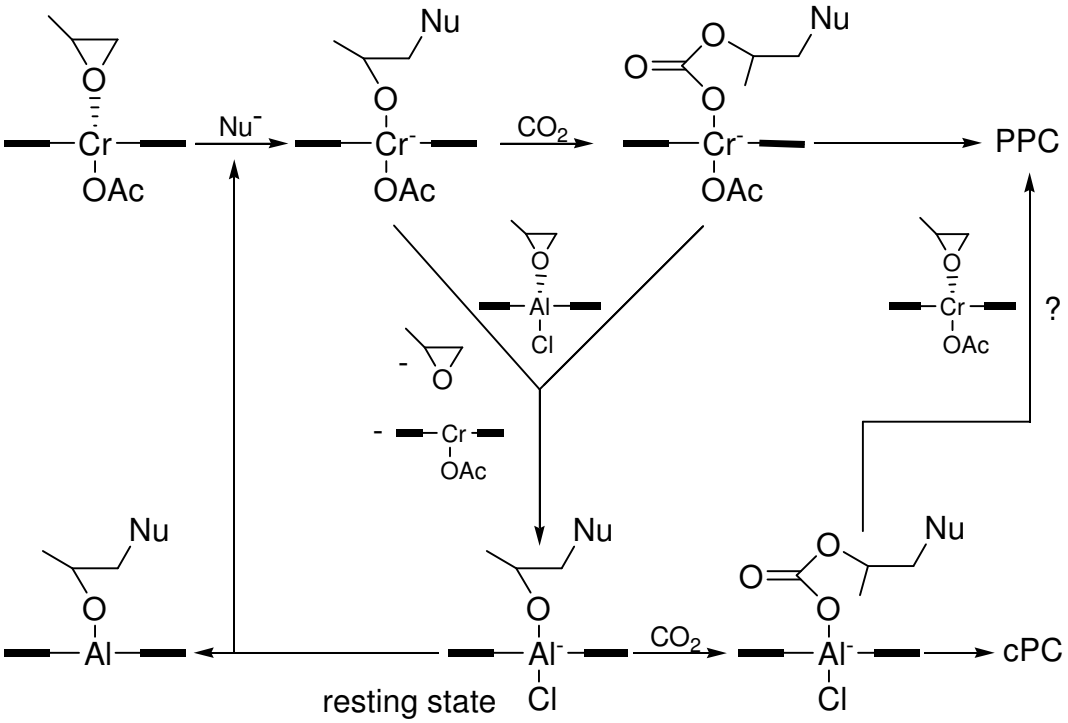


Figure 5 **PO/CO_2 conversion mediated by mixtures of chromium(III)-salophen-acetate and aluminium(III)-salophen-chloride complexes at 35 bar CO_2 pressure, 75 °C and 2 hours reaction time.**

In addition, the quantity of converted PO corresponds to the amount expected for catalysis by chromium(III)-salophen-acetate within the error margin. Thus, all converted PO was activated and attacked at chromium(III) (as function of the average nucleophile binding at the metal centre), and formation of cPC was supported by both chromium(III)-salophen-acetate and aluminium(III)-salophen-chloride. Consistent with this interpretation, an analysis of the microstructure of the PPC formed by the action of mixtures of chromium(III) and aluminium(III)-salophen complexes shows the same regiochemistry as PPC obtained from chromium(III)-salophen alone (head-to-tail approximately 76%). This indicates that a polycarbonate formation (epoxide ring-opening) occurs predominantly at chromium(III). The Lewis acidity has a marked impact on the regiochemistry.[11,12] Scheme 8 shows the interactions during the catalytic cycle between chromium(III)-salophen-acetate and aluminium(III)-salophen-chloride complexes as discussed above.



Scheme 8 **Interactions during the catalytic cycle between chromium(III)-salophen-acetate and aluminium(III)-salophen-chloride complexes.**

If the interaction described in Scheme 8 is the dominant process, the molecular weights should decrease and the distribution should be broadened, implying that the decomposition of the chain end becomes an important reaction. This is indeed observed (Table 5), also as function of the amount of aluminium present.

Entry	$n(Cr^{III})$ [µmol]	$n(Al^{III})$ [µmol]	M_n [gmol^{-1}]
1	45,5	0	13400
2	45,5	45,5	7200
3	45,5	136,5	5986

Table 5 **Analysis of the resulting polycarbonates of copolymerisation experiments with mixtures of chromium(III)-salophen-acetate and aluminium(III)-salophen-chloride complexes and 1 equiv. of tetrabutyl ammonium chloride at 35 bar CO_2 pressure, 75°C and 2 hours reaction time.**

This leads to a consistent picture. The stronger, more effective Lewis acid chromium(III)-salophen-acetate activates the epoxide for nucleophilic attack. The nucleophiles at aluminium(III) must mainly appear as alkoxide, since carbonates are not stable toward dissociation. Being more or less unable to react effectively with chromium(III)-coordinated epoxides and decrease the PO rate of conversion. This demonstrates the fact that CO_2 insertion is the rate-determining step for cPC formation mediated by aluminium(III)-salophen species.

The remaining question concerns the mode of nucleophile exchange between chromium(III)- and aluminium(III)-salophen complexes. Does the nucleophilic attack occur on an aluminium(III)-coordinated epoxide through an chromium(III)-alkoxide or –carbonate moiety? However, the more favourable pathway is the latter one.

As already found via DFT calculations, performed by Dr. F. Molnar, for the initiation reaction in the chromium(III)-salophen-acetate species an attractive route could not be detected for a *syn* insertion of the epoxide at a single metal centre, which does not have a five-coordinate geometry.[†] However, a comparable alternative low-energy pathway was detected as soon as reactions between chromium(III)-salophen-carbonate complex and a second metal centre carrying an activated epoxide were allowed. In the productive step, the carbonate group was transferred from one metal centre to the epoxide carbon atom carried by the other. During this formal chain- or metal-exchange process the epoxide undergoes ring-opening and is incorporated into the polymer chain leading to an alkoxy group at the second metal centre. The process is depicted in Figure 6.

[†] Calculations were performed on the basis of an unsubstituted chromium(III) complex species having an ethylene diimine bridged salen ligand.

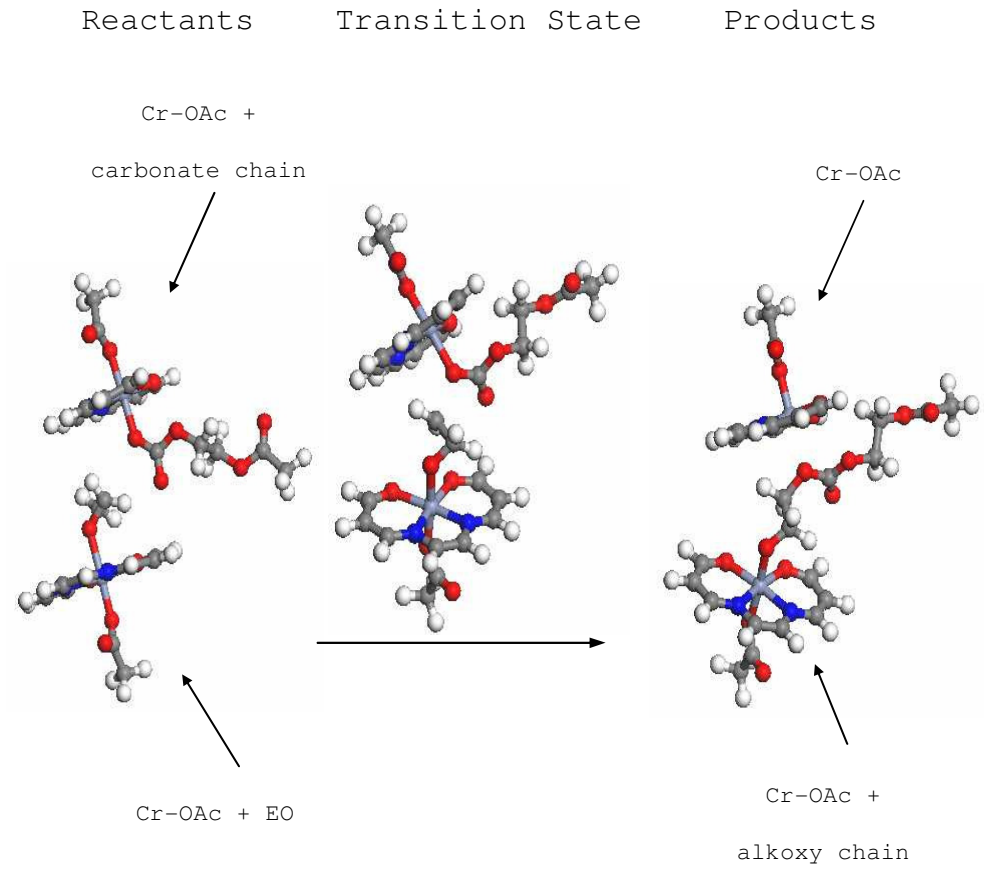


Figure 6 **Chain transfer and growth, a carbonate chain end group is transferred and ring-opens an activated epoxide. Acetate ligands in the *trans* position.[13]**

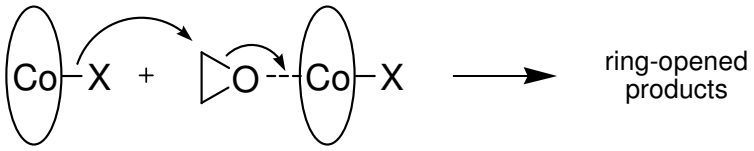
The attack may proceed either with the C=O moiety or with the carbonate-metal-oxygen atom (C-O). They show slightly different activation energies but all within a plausible range for reaction to occur at ambient temperatures. Details of the transfer mechanisms are given in Table 6. The activation barrier was also determined for the formation of a polyether, that is, the corresponding attack of chromium(III)-bound alkoxide at a coordinated epoxide. This process has a somewhat lower activation barrier and a more negative enthalpy. Polyether formation in the case of chromium(III)-salophen catalysis may thus be expected to be competitive at low carbon dioxide concentration. Moreover, the effect of high- and low-spin states of both centres of two chromium(III)-salophen-acetate complexes on the reactivity has been studied. From the data collected in Table 6 it becomes clear that there is no strong dependence on spin state. For the alkoxide transfer no transition state could be located on the triplet surface.

	Septet		Quintet		Triplet	
	$\Delta E^{\#}$ [kJ/mol]	ΔE [kJ/mol]	$\Delta E^{\#}$ [kJ/mol]	ΔE [kJ/mol]	$\Delta E^{\#}$ [kJ/mol]	ΔE [kJ/mol]
carbonato (-O)	51	8	39	-13	41	-12
carbonate (=O)	28	-23	32	-22	29	-30
alkoxide (-O)	16	-72	22	-72	-	-

Table 6 **Activation barriers ($\Delta E^{\#}$) and reaction enthalpies (ΔE) for chain transfer reaction (ring-opening) between two chromium(III)-salophen-acetate complexes.**

4.3.1 EFFECT OF TRANS LIGAND

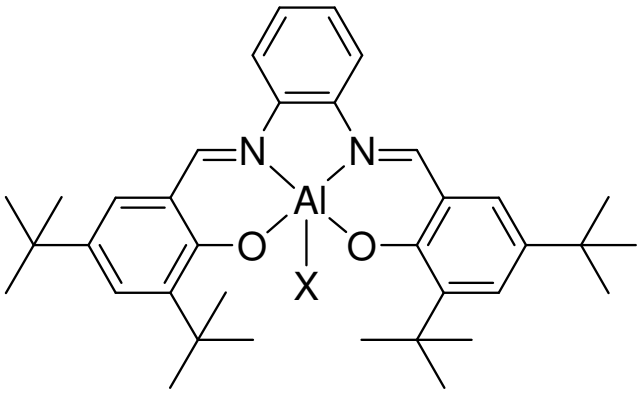
Jacobsen and co-workers conducted extensive studies that support a bimetallic mechanism for the chiral cobalt(III)-salcy-X[‡] catalysed kinetic resolution of terminal epoxides (Scheme 9).[14]



Scheme 9 **Bimetallic cobalt(III)-salcy-X (X = nucleophile) ring-opening proposed by Jacobsen et al.[14]**

With these systems they observed a large reaction rate dependence on the composition of the axial ligand (X) of the catalyst. These results supported our assumption that the nature of the *trans* ligand would likewise influence the rate of the copolymerisation of propylene oxide and carbon dioxide. We investigated this impact by varying the axial ligand of aluminium(III)-salophen complexes (Scheme 10).

[‡] salcy = N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexane; X = halide or carboxylate



X = Cl, Et, OAc, OPh

Scheme 10 Aluminium(III)-salophen complexes with different axial ligand for the copolymerisation of propylene oxide and CO_2.

Table 7 presents the copolymerisation results obtained with equimolar amounts of the aluminium(III)-salophen catalyst and NBu_4Cl in 3000 equivalents of propylene oxide and at 14 bar CO_2 pressure. All experiments were carried out at 75°C and four hours reaction time. Results given are overall results for this reaction period.

As expected for the application of aluminium(III) as active centre, the cyclic propylene carbonate (cPC) is produced exclusively in all experiments. This means that neither polycarbonate nor polyether linkages could be observed. The anion de-coordination reaction is especially easy in aluminium(III)-salophen complexes. It seems that the decomposition of the carbonate species is the fastest reaction in the system: chain propagation to yield PPC appears not competitive with the backbiting. Even if small chains were formed, total decomposition of intermediate (poly)carbonate chains is very efficient as soon as the carbonate anion is liberated from the metal centre.

Metal-salophen complex	NBu_4Cl (equiv./cat.)	PO (equiv./cat.)	PO conversion	Equiv. PO in cPC	TOF cPC [h^{-1}]
Al(III)-Cl	1	3000	1194	1194	300
Al(III)-Et	1	3000	738	738	185
Al(III)-OAc	1	3000	75	75	19
Al(III)-OPh	1	3000	873	873	219

Table 7 **Effect of the axial ligand of several aluminium(III)-salophen catalysts for the copolymerisation of propylene oxide and CO_2 at 75 °C and four hours reaction time.**

The activation (polarisation) of the epoxide is affected by the nature of the *trans* ligand, as the effective Lewis acidity is a function of the electron-withdrawing character of this group. The stronger these character the higher the resulting copolymerisation activity of the system.

4.3.2 EFFECT OF TEMPERATURE

As known, the conversion of epoxides strongly increases with higher temperatures.[15] We can verify this dependence with the results of all of our investigated systems. Table 8 presents the copolymerisation results obtained with a 1:1 mixture of chromium(III)-salophen-acetate and aluminium(III)-salophen-ethyl catalysts. The experiments were performed at different temperatures but otherwise with constant conditions (3000 equiv. PO, 1 equiv. NBu_4Cl, 14 bar CO_2, 4 h) (Figure 7).

Temperature [°C]	total PO conversion	Equiv. PO in PPC	Equiv. PO in cPC
65	675	597	63
75	1653	1179	453
85	2268	1275	849

Table 8 **PO conversion (3000 equivalents) on 14 bar CO_2 pressure and 4 hours reaction time mediated by chromium(III)-salophen-acetate, aluminium(III)-salophen-ethyl and tetrabutyl ammonium chloride (1:1:1) as function of temperature.**

The overall consumption of propylene oxide shows a strong dependence on the reaction temperature. The higher the temperature, the higher is the conversion rate. The formation of cyclic propylene carbonate (cPC) shows a nearly linear dependence on the temperature. Higher temperatures lead to higher cPC formation. However, the increase of the poly(propylene carbonate) production (PPC) is at lower temperatures (65-75°C) much more distinctive than at higher (75-85°C). This behaviour led us to the presumption that at higher temperatures (like 100°C) the cPC formation should be the dominant reaction. This indicates the assumed depolymerisation process starting from a dissociated polymer chain (compare backbiting mechanism). It is obvious that increased temperatures support the dissociation of a carbonate chain end from the metal centre and, hence, effect enhanced formation of cyclic propylene carbonate.

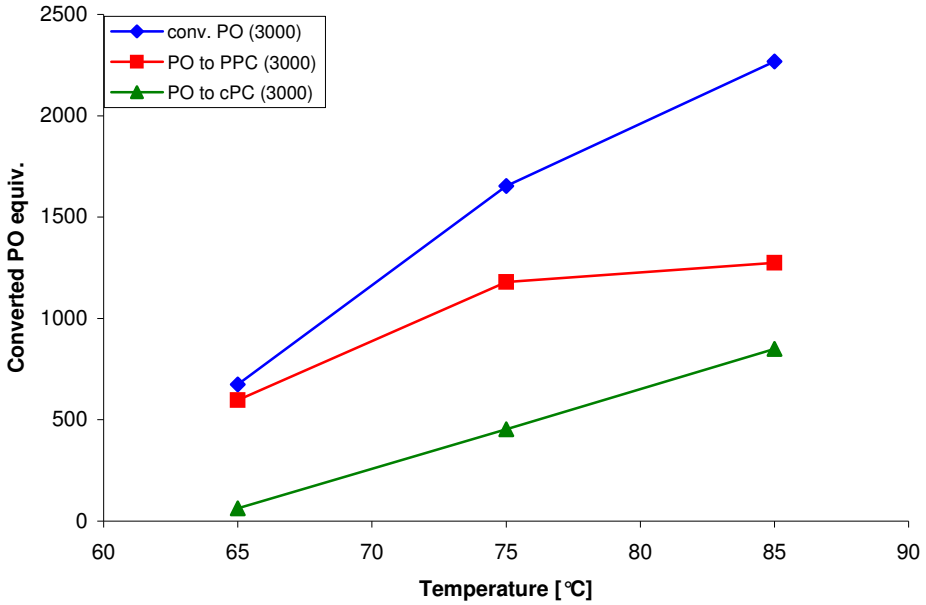


Figure 7 **Temperature dependency of the copolymerisation reaction with chromium(III)-salophen-acetate and aluminium(III)-salophen-ethyl as catalysts.**

4.3.3 EFFECT OF CATALYST/CO-CATALYST RATIO

The catalyst/co-catalyst ratio has already been identified as the main factor for controlling the carbonate product distribution in the DMAP-assisted copolymerisation reaction.[16] Generally, less than one equivalent of co-catalyst promotes the formation of poly(propylene carbonate). Similar results were obtained in our system, in which a 1:1 mixture of chromium(III)-salophen-acetate and aluminium(III)-salophen-ethyl was used together with tetrabutyl ammonium chloride as co-catalyst. The experiments were performed under constant conditions (3000 equiv. PO, 14 bar CO_2, 75°C, 4 h) but with different amounts of the co-catalyst (Table 9, Figure 8).

Interestingly, the reaction applying 2 equivalents NBu_4Cl afforded not only cPC, as observed in the DMAP-assisted reactions, but also about 11% polycarbonate.

Equiv. NBu_4Cl	total PO conversion	Equiv. PO in PPC	Equiv. PO in cPC	% carb. linkage
0.5	1431	984	270	88
1	1653	1179	453	99
2	2085	219	1851	99

Table 9 **PO conversion (3000 equivalents) at 75°C, 14 bar CO_2 pressure and 4 hours reaction time mediated by chromium(III)-salophen-acetate, aluminium(III)-salophen-ethyl (1:1) as function of the tetrabutyl ammonium chloride ratio.**

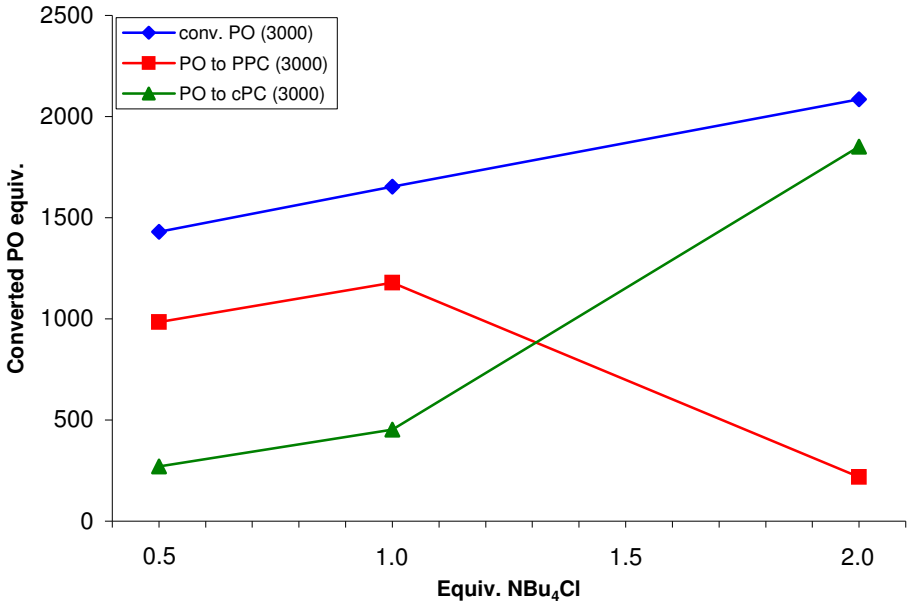
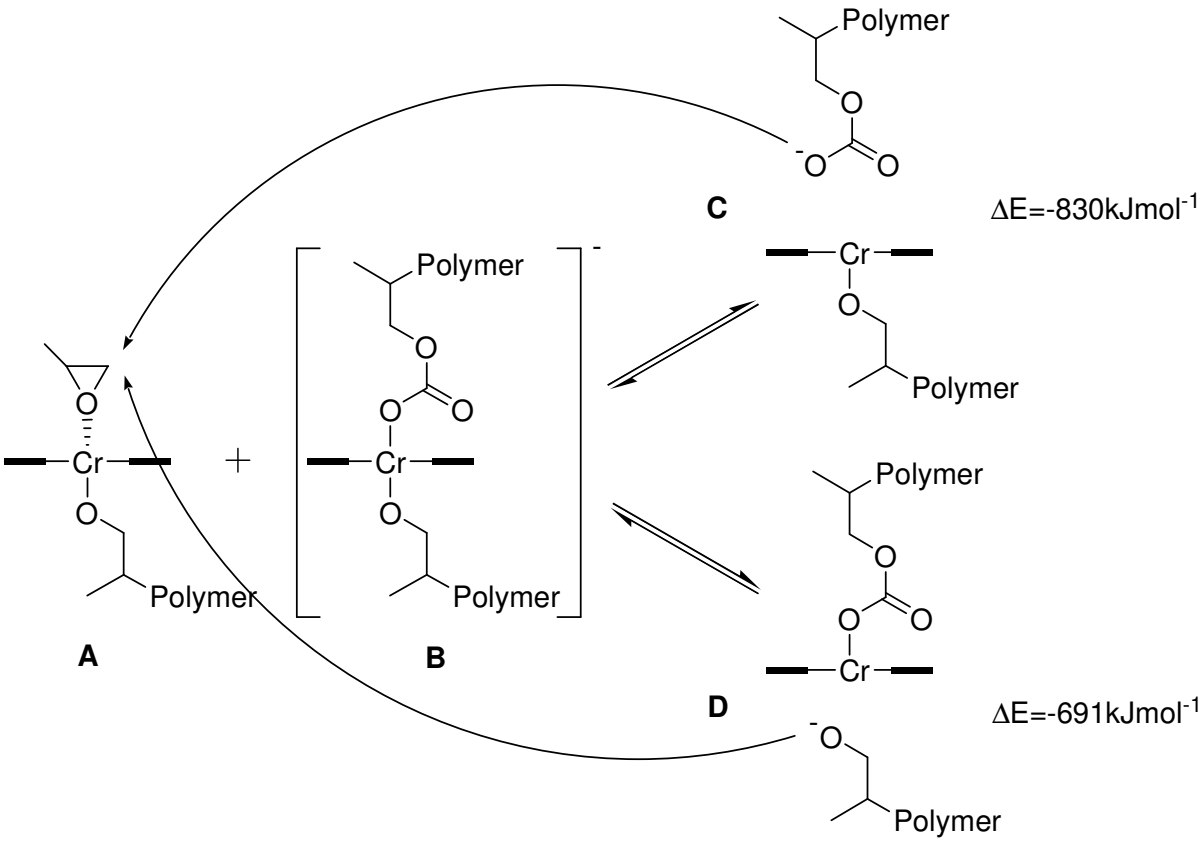


Figure 8 **Dependency on the catalyst/co-catalyst ratio of the copolymerisation reaction mediated by chromium(III)-salophen-acetate and aluminium(III)-salophen-ethyl catalysts.**

In accordance with DMAP-assisted reactions depolymerisation decreases when applying catalyst/co-catalyst ratios are less than one. Under these conditions, two chromium(III)-salophen species are present, with either one **(A)** or two **(B)** coordinated polymer chains (Scheme 11). Generally, backbiting was found to be possible in the case of a dissociated carbonate or alcoholate species.[13] DFT calculations showed dissociation of a polymer chain to be energetically favoured in the case of chromium(III)-salophen species carrying two polymer chains. Reduction of catalyst/co-catalyst ratio corresponds with a decreased concentration of species **B**. Reduced cPC formation at lower catalyst/co-catalyst ratio is obvious. The reduction of the total conversion of propylene oxide goes along with decreased co-catalyst concentration indicates that **A** is a dormant species. It is not able to undergo epoxide ring-opening without a present nucleophile (chloride or carbonate/alcoholate chain end).

The increased formation of ether linkages (small rate of carbonate linkages, Table 9) when applying low catalyst/co-catalyst ratios can be explained by a high concentration of species **A**. Therefore, chain transfer of an alcoholate to **A** becomes more likely. The fact that an ether bond formation is almost suppressed at high catalyst/co-catalyst ratios suggests that species **D** (free alcoholate chain end) does not undergo chain growth via epoxide ring-opening.



Scheme 11 Possible reaction routes using catalyst/co-catalyst ratios less than one.

4.3.4 EFFECT OF CO_2 PRESSURE

The product distribution of the copolymerisation reaction shows a strong dependence on the CO_2 pressure (Table 10, Figure 9). In our catalytic system we used equimolar amounts of the chromium(III)-salophen-acetate and aluminium(III)-salophen-ethyl catalysts. All experiments were performed under constant conditions (3000 equiv. propylene oxide, 1 equiv. tetrabutyl ammonium chloride, 75°C, 4 h) but different carbon dioxide pressures.

CO_2 [bar]	total PO conversion	Equiv. PO in PPC	Equiv. PO in cPC	% carb. linkage
7	1485	792	636	96
14	1653	1179	453	99
25	1194	783	411	100

Table 10 **PO conversion (3000 equivalents) at 75°C and 4 hours reaction time mediated by chromium(III)-salophen-acetate, aluminium(III)-salophen-ethyl and tetrabutyl ammonium chloride (1:1:1) as function of the carbon dioxide pressure.**

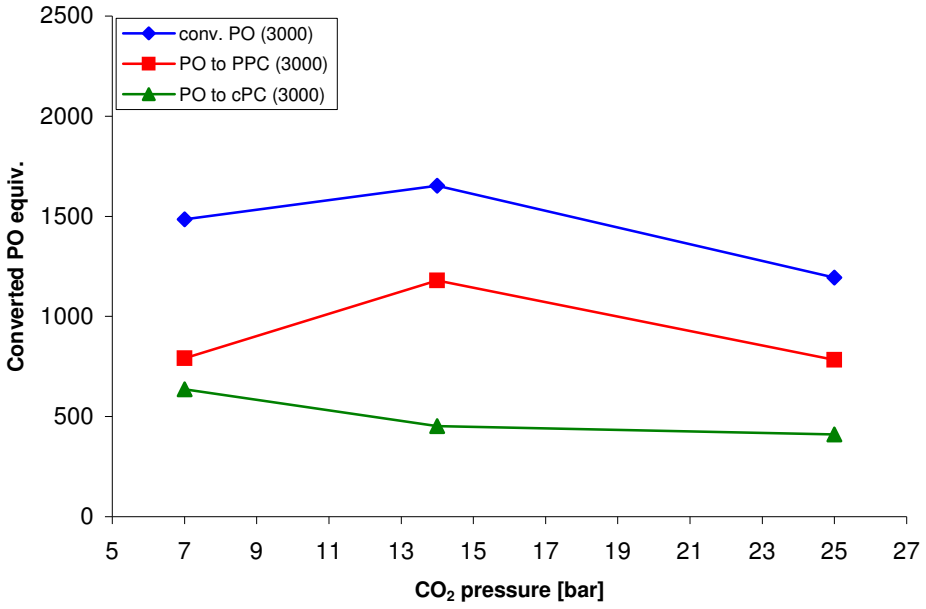
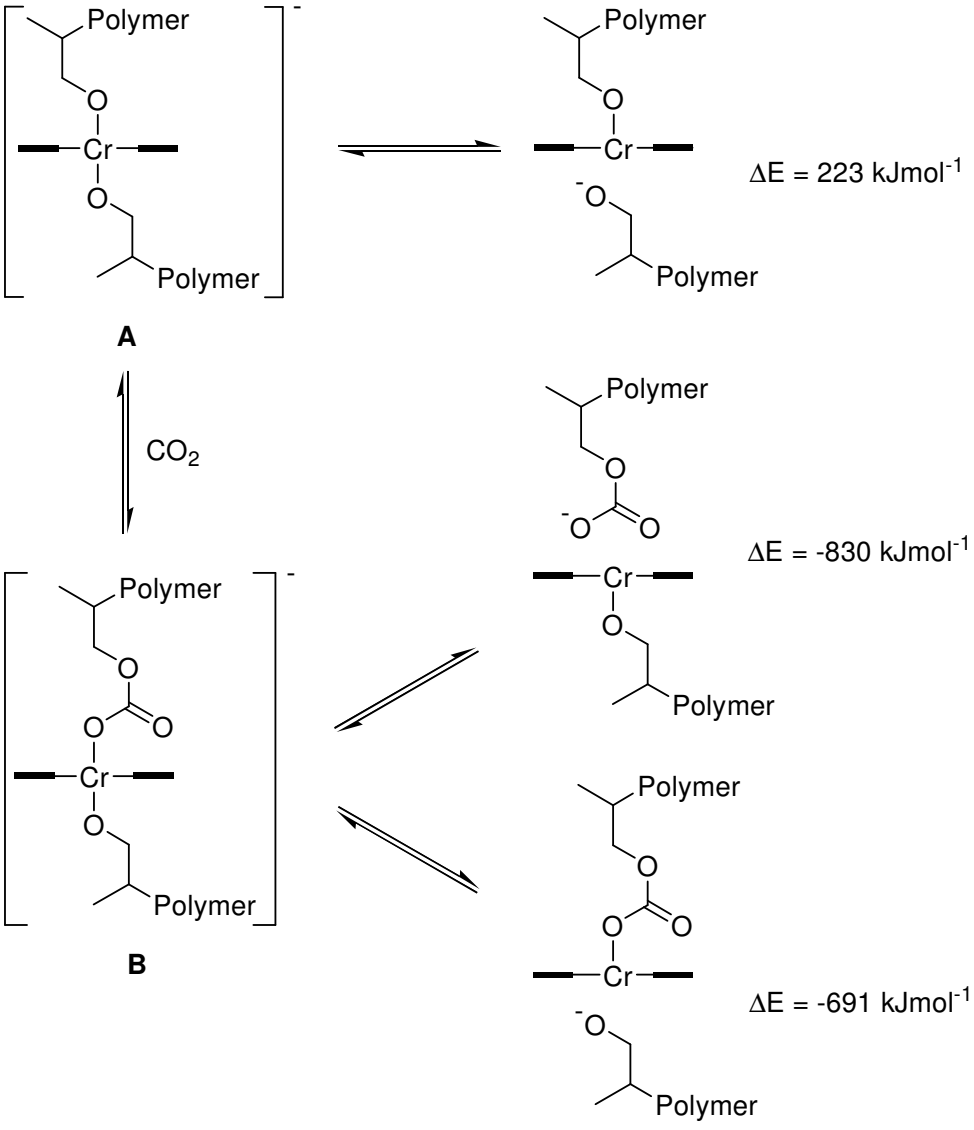


Figure 9 **Dependency on the CO_2 pressure of the copolymerisation reaction mediated by chromium(III)-salophen-acetate and aluminium(III)-salophen-ethyl catalysts.**

Although the formation of cyclic propylene carbonate is more or less independent of the CO_2 concentration, the polycarbonate production goes through a clear maximum at 14 bar. This effect may be explained on the basis of the CO_2 insertion step presented in Scheme 12. The ratio between species **A** and species **B** is directly influenced through the CO_2 pressure. **A** should be the predominant species at low CO_2 pressures while the rate of **B** should increase with the CO_2 concentration. Precisely because the formation of cPC seems to be independent of the CO_2 pressure, depolymerisation can be expected to occur not only via backbiting of a carbonate chain end but also via an alcoholate species. However, this is not consistent with calculated dissociation energies, which indicate alcoholate dissociation from **A** to be highly disfavoured.

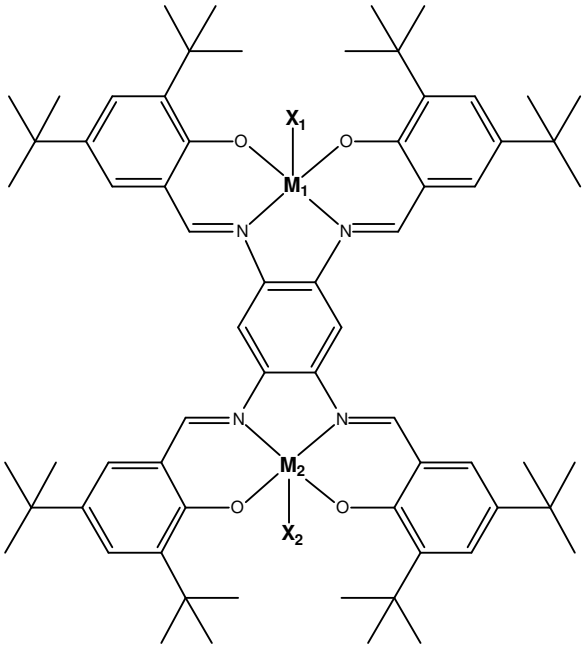


Scheme 12 Dependency of the cPC formation on the CO_2 pressure.

4.4 SPECIAL CATALYSTS

4.4.1 BINUCLEAR CHROMIUM(III)- AND ALUMINIUM(III)-SALOPHEN COMPLEXES

In order to optimise the chain transfer between two catalytic active species we investigated some new binuclear complexes with either chromium(III) or aluminium(III) metal centres (Scheme 13). This kind of ligand structure ensures that two centres are always close together. Thus, the period in which the carbonate chain end is searching an activated epoxide, should be much shorter than in case of two mononuclear salophen complexes and therefore, the overall activity of the copolymerisation should strongly increase.



C12 $M_1 = M_2 = Cr$, $X_1 = X_2 = OAc$

C13 $M_1 = M_2 = Al$, $X_1 = X_2 = Cl$

C16 $M_1 = Cr$, $M_2 = Al$, $X_1 = OAc$, $X_2 = Cl$

Scheme 13 New binuclear complexes for the synthesis of aliphatic polycarbonates.

We have shown that the formation of cyclic propylene carbonate (cPC), being equal to chain degradation, takes place predominantly via a backbiting mechanism of a free carbonate chain end. So another positive aspect in case of a fast chain transfer is that the time period of a free carbonate chain end is very short. Therefore, the determining side reaction, formation of cPC, is suppressed

and the formation of PPC is even more predominant than in systems with mononuclear salophen catalysts.

RESULTS AND DISCUSSION

A first set of experiments concerned the reactivity of complex **C12** (Scheme 13) and epoxide/CO_2. These experiments were carried out in neat propylene oxide, at 75°C and four hours reaction time (Table 11). In general both poly(propylene carbonate) and cyclic propylene carbonate are formed at the same time.

Entry	NBu_4Cl (equiv./cat.)	CO_2 [bar]	PO (equiv./cat.)	total PO conv.	Equiv. PO in PPC	% PPC	Equiv. PO in cPC	% carb. linkage	T [°C]
1	2	14	6000	510	66	13	408	93	**50**
2	2	14	6000	1410	216	15	930	81	**75**
3	2	14	6000	3372	0	0	2772	82	**100**
4	2	**7**	3000	1569	168	11	996	74	75
5	2	**14**	3000	1497	492	33	666	77	75
6	2	**25**	3000	1980	630	32	840	74	75
7	**0.5**	14	1500	716	357	50	101	64	75
8	**1**	14	1500	1181	602	51	198	68	75
9	**2**	14	1500	1422	492	35	444	66	75
10	**0.5**	14	3000	480	228	48	81	64	75
11	**1**	14	3000	840	441	53	114	66	75
12	**2**	14	3000	1497	492	33	666	77	75
13	**0.5**	14	6000	414	204	49	54	62	75
14	**1**	14	6000	732	330	45	144	65	75
15	**2**	14	6000	1410	216	15	930	81	75
16	**0.5**	14	**1500**	716	357	50	101	64	75
17	**0.5**	14	**3000**	480	228	48	81	64	75
18	**0.5**	14	**6000**	414	204	49	54	62	75
19	**1**	14	**1500**	1181	602	51	198	68	75
20	**1**	14	**3000**	840	441	53	114	66	75
21	**1**	14	**6000**	732	330	45	144	65	75
22	**2**	14	**1500**	1422	492	35	444	66	75
23	**2**	14	**3000**	1497	492	33	666	77	75
24	**2**	14	**6000**	1410	216	15	930	81	75

Table 11 Experiments with complex C12 (45.5 µmol) and 4 hours reaction time.

The amount of the external nucleophile (chloride) has a distinctive impact on the product distribution. Increasing the equivalents of chloride relative to complex **C12** leads to increased formation of cPC. At a ratio larger than one it becomes the dominant product. The PPC formed generally has a carbonate linkage content of only 60 to 80%. Thus, the polymer includes a high amount of ether linkages, this shows a clear contrast to mononuclear salophen catalysts (at similar copolymerisation conditions over 95% of carbonate linkages were observed).

The concentration of carbon dioxide shows a marked impact on the formation of PPC at low CO_2 pressures but more or less no impact on the content of carbonate linkages of the polymer chain (always about 75% carbonate linkages).

The influence of the catalyst concentration is more complicated. In low amounts of additional external nucleophiles, the formation of PPC and the content of carbonate linkages are more or less independent of the dilution of the catalyst (Table 11, entries 16-18). But at higher amounts of external nucleophiles the formation of PPC decreases dramatically by increasing the dilution. Especially in the system with 6000 equivalents PO and 2 equivalents external chloride the polymer production is strongly suppressed and the formation of cyclic propylene carbonate is the dominant process (Table 11, entry 24).

A second set of experiments was performed with complex **C13** (Scheme 13). The experiments were again carried out in neat propylene oxide, at 75°C and four hours reaction time (Table 12). The cyclic propylene carbonate is produced exclusively, poly(propylene carbonate) was observed in none of the experiments. This is similar to catalysis with mononuclear aluminium(III)-salophen-chloride as catalyst where also no polymer could be produced.

Entry	NBu_4Cl (equiv./cat.)	CO_2 [bar]	PO (equiv./cat.)	total PO conv.	Equiv. PO in PPC	% PPC	Equiv. PO in cPC	% carb. linkage	T [°C]
1	2	14	6000	456	0	0	456	100	**50**
2	2	14	6000	1362	0	0	1362	100	**75**
3	2	14	6000	1782	0	0	1782	100	**##**
4	1	14	**1500**	914	0	0	914	100	75
5	1	14	**3000**	669	0	0	669	100	75
6	1	14	**6000**	834	0	0	834	100	75
7	2	14	**1500**	1185	0	0	1170	99	75
8	2	14	**3000**	1347	0	0	1347	100	75
9	2	14	**6000**	1362	0	0	1362	100	75
10	2	**7**	3000	1224	0	0	1224	100	75
11	2	**14**	3000	1347	0	0	1347	100	75
12	2	**25**	3000	1527	0	0	1527	100	75
13	2	**7**	6000	1110	0	0	1110	100	75
14	2	**14**	6000	1362	0	0	1362	100	75
15	2	**25**	6000	1452	0	0	1452	100	75

Table 12 Experiments with complex C13 (45.5 µmol) and 4 hours reaction time.

The activity of the catalyst shows a nearly linear dependence on the CO_2 pressure (Table 12, entries 10-12). Increasing the pressure of carbon dioxide leads to an increased conversion of propylene oxide. In a more diluted system, the activity increases again by raising the pressure but the overall PO conversion is slightly lower than before (Table 12, entries 13-15).

The influence of the dilution of the catalyst shows a different behaviour either if one or two equivalents of external chloride are added (Table 12, entries 4-9). In the system with one equivalent chloride the activity goes through a minimum at 3000 equivalents of propylene oxide. Unexpectedly, the highest activity could be reached in the system with 1500 equivalents of PO. This is contrary to the catalytic system with mononuclear aluminium(III)-salophen complexes where the activity increases by raising the dilution. The system with two equivalents external chloride shows the “normal” dependence on the dilution, but there is more or less no influence between the system with 3000 and 6000 equivalents PO observed.

A third set of experiments was performed with a catalyst system were the binuclear complex combines both one active chromium(III) and one active aluminium(III) centre (complex **C16**, Scheme 13). Again, the experiments were carried out in neat propylene oxide, at 75 °C and four hours reaction time (Table 13).

Entry	NBu_4Cl (equiv./cat.)	CO_2 [bar]	PO (equiv./cat.)	total PO conv.	Equiv. PO in PPC	% PPC	Equiv. PO in cPC	% carb. linkage	T [°C]
1	2	14	**1500**	1500	0	0	1500	100	75
2	2	14	**3000**	2592	138	5	2385	97	75
3	2	14	**6000**	3336	0	0	3336	100	75
4	2	**7**	3000	2118	0	0	2118	100	75
5	2	**14**	3000	2592	138	5	2385	97	75
6	2	**25**	3000	2106	285	14	1737	96	75

Table 13 Experiments with complex C16 (45.5 µmol) and 4 hours reaction time.

The influence of CO_2 pressure shows an interesting behaviour (Table 13, entries 4-6). The overall activity of the system goes through a maximum at 14 bar CO_2 but the formation of poly(propylene carbonate) shows a nearly linear dependence on the CO_2 pressure. Higher CO_2 concentrations lead to increased PPC formation. At low CO_2 pressure no polymer could be obtained. Obviously, the polycarbonate formation is only the minor process in this system. The formation of cyclic carbonate is the dominant reaction.

This system shows a complete new dependence on the amount of the epoxide (Table 13, entries 1-3). In contrast to the systems with complexes **C12** and **C13**, now the activity strongly depends on dilution of the catalyst. By raising the epoxide amount the total conversion of PO drastically increases. The overall activity is extremely higher than in the other systems (factor of 1.7 with 3000 equivalents PO and 2.3 with 6000 equivalents PO).Only in the system with 3000 equivalents of propylene oxide a polymer formation could be observed. The formation of cyclic carbonate is again the dominant process.

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CHAPTER 5

SYNTHESIS

5.1 INTRODUCTION

This chapter contents the descriptions of the syntheses of all new and non-commercial compounds which were used in the presented work. Using conventional Schlenk techniques under dry argon atmosphere, all air and moisture sensitive manipulations were carried out. The glassware was dried at 80°C in vacuum prior to use. The solvents were dried by distillation employing different drying agents and were stored over molecular sieves under an argon atmosphere (Table 1). The water content was determined by Karl-Fischer titration and was in all cases below 12 ppm. All commercial materials were obtained from Fluka, Merck and Sigma-Aldrich, Lancaster and ABCR, and, if not otherwise mentioned, were used without further purification.

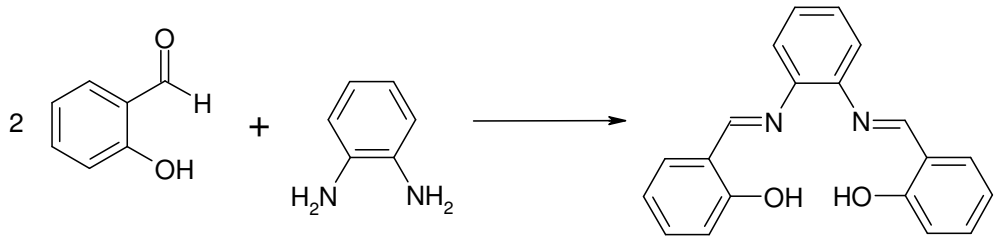
Solvent	Drying agent	Molecular sieve
THF	$LiAlH_4$	4 Å
CH_2Cl_2	CaH_2	4 Å
toluene	$LiAlH_4$	4 Å
diethyl ether	$LiAlH_4$	4 Å
hexane	$LiAlH_4$	4 Å
methanol	Mg	3 Å

Table 1 Drying agents used for solvents.[1]

All ^1H NMR and ^{13}C NMR measurements were recorded on a Bruker DRX400 spectrometer. Chemical shifts δ are given in ppm in reference to signals of the deuterated solvents. Infrared (IR) spectra were obtained on KBr pellets using a Bruker IFS 113V and IFS 66V instrument. Elemental analyses were determined in the department of Analytical and Environmental Chemistry, University of Ulm. MS MALDI measurements were performed on a Bruker Daltonics REFLEX III (Department of Mass Spectroscopy, University of Ulm) with anthralin as matrix.

5.2 SYNTHESIS OF LIGANDS AND COMPLEXES

Salophen (salicylidene-1,2-phenylene diimine) ***L1****:*

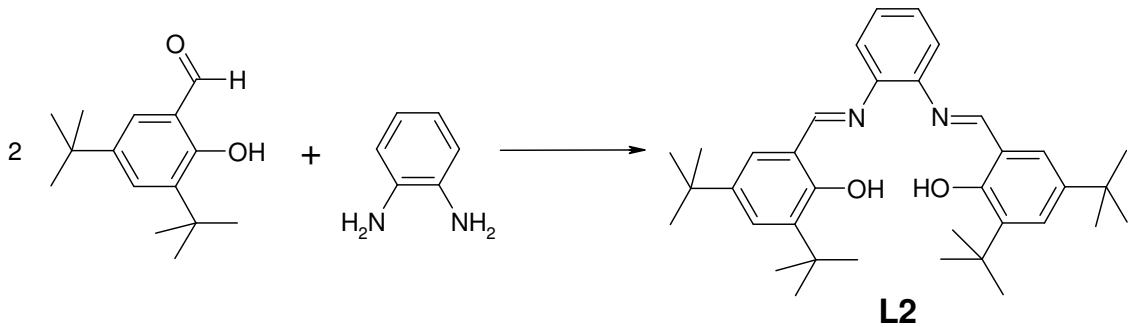


L1

1,2-phenylene diamine (3.5 g, 32.5 mmol) was dissolved in anhydrous ethanol (140 ml). To the solution was added dropwise salicylaldehyde (7.8 g, 64 mmol) and stirred under reflux for 4 hours. The solution was allowed to cool to room temperature and the precipitate was filtered off and washed with cooled ethanol. The product was dried under high vacuum to yield 9.5 g (91 %) as orange needles.

M.p. 165.1°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.0 (s, 2 H), 8.6 (s, 2 H), 7.4-6.9 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.72, 161.39, 142.53, 133.40, 132.41, 127.74, 119.73, 119.22, 119.10, 117.55. IR (KBr) (cm^{-1}): 3052, 2923, 2853, 1613, 1585, 1560, 1479, 1448, 1401, 1363, 1275, 1232, 1190, 1149, 1110, 1042, 996, 975, 938, 908, 885, 856, 828, 809, 788, 758, 637, 578, 553, 527, 498, 468, 436, 415. Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.85. Found: C, 75.78; H, 5.11; N, 8.78.

Tetra-tert-butyl-salophen (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine) ***L2****:*

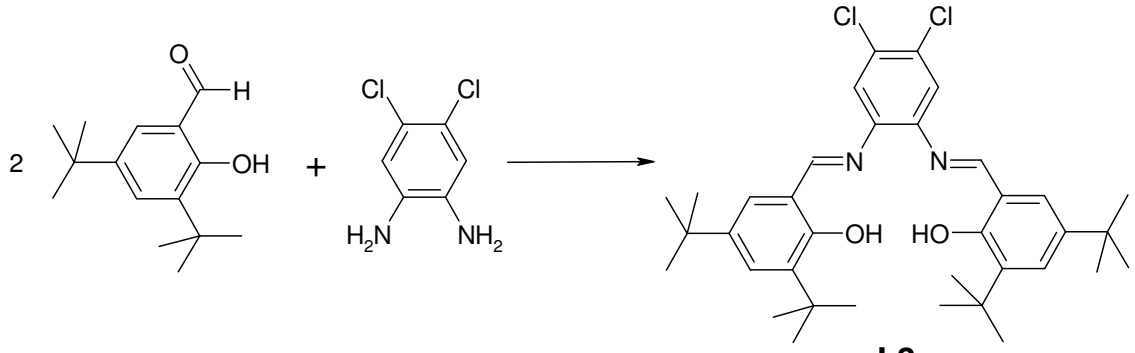


L2

3,5-di-*tert*-butylsalicylaldehyde (5.0 g, 21.3 mmol) and 1,2-phenylene diamine (1.1 g, 10.0 mmol) were refluxed in anhydrous ethanol (40 ml) for 4 hours. The yellow solution was allowed to cool to room temperature and the precipitate was filtered off and washed with cooled ethanol. The product was dried under high vacuum to yield 4.8 g (89 %) as yellow needles.

M.p. 192.6°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.5 (s, 2 H), 8.7 (s, 2 H), 7.4-7.2 (m, 8 H), 1.4 (s, 18 H), 1.3 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.71, 158.58, 142.75, 140.31, 137.20, 128.16, 127.29, 126.76, 119.80, 118.37, 35.12, 34.15, 31.47, 29.45. IR (KBr) (cm^{-1}): 2956, 2906, 2867, 1616, 1572, 1481, 1438, 1392, 1362, 1323, 1275, 1251, 1230, 1200, 1170, 1104, 1027, 975, 932, 878, 851, 823, 776, 756, 680, 643, 539, 500. Anal. Calcd for $C_{36}H_{48}N_2O_2$: C, 79.69; H, 8.95; N, 5.18. Found: C, 79.74; H, 8.93; N, 5.21.

Tetra-tert-butyl-dichloro-salophen (N,N'-bis-(3,5-di-tert-butylsalicylidene)-4,5-dichloro-1,2-phenylene diimine) ***L3****:*

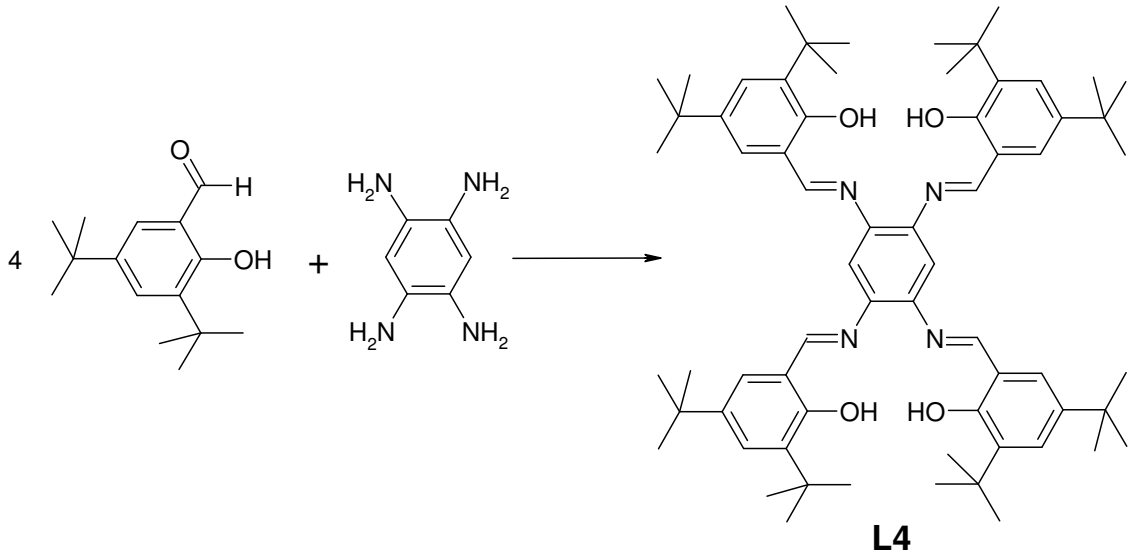


L3

3,5-di-*tert*-butylsalicylaldehyde (5.0 g, 21.3 mmol) and 4,5-dichloro-1,2-phenylene diamine (1.8 g, 10.2 mmol) were dissolved in anhydrous ethanol (70 ml) and heated under reflux for 8 hours. The solution was allowed to cool to room temperature and left for 24 hours. The precipitate was filtered off and washed with cooled ethanol. The product was dried under high vacuum to yield 5.1 g (82 %) as brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 13.1 (s, 2 H), 8.6 (s, 2 H), 7.5 (s, 2 H), 7.4 (s, 2 H), 7.2 (s, 2 H), 1.4 (s, 18 H), 1.3 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.64, 158.73, 142.23, 140.74, 137.31, 130.52, 128.97, 127.13, 121.22, 118.05, 35.12, 34.16, 31.44, 29.42. IR (KBr) (cm^{-1}): 2957, 2907, 2868, 1612, 1592, 1567, 1469, 1437, 1392, 1359, 1324, 1270, 1248, 1201, 1174, 1150, 1026, 981, 929, 881, 828, 803, 771, 755, 725, 684, 641, 537, 490, 435. Anal. Calcd for $C_{36}H_{46}Cl_2N_2O_2$: C, 70.92; H, 7.60; N, 4.59. Found: C, 69.60; H, 7.46; N, 4.63.

Bis-salophen (N',N'',N''',N''''-tetra-(3,5-di-tert-butylsalicylidene)-1,2,4,5-phenylene tetraimine) ***L4****:*

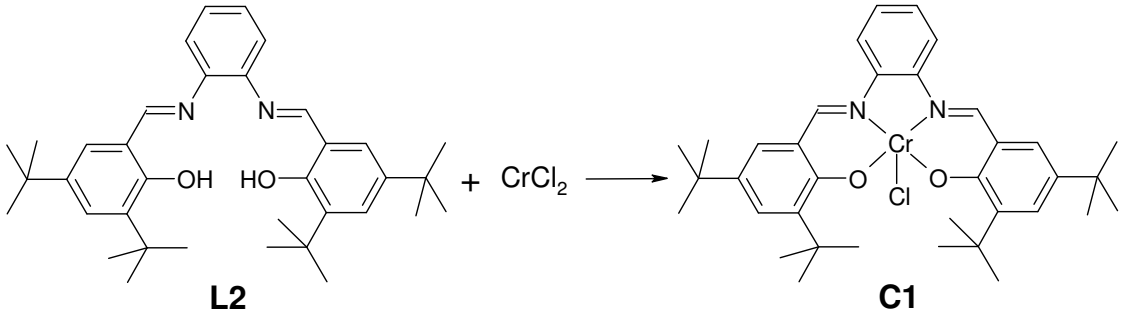


L4

3,5-di-*tert*-butylsalicylaldehyde (5.0 g, 21.3 mmol) and 1,2,4,5-benzenetetraamine tetrahydrochloride (1.25 g, 4.4 mmol) were heated in anhydrous EtOH (50 ml) under reflux for 18 h. The solution was cooled to 0°C and stirred for 3 h. The yellow-orange precipitate was filtrated, washed with cooled anhydrous EtOH and dried under high vacuum to yield 3.4 g (77 %).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 13.5 (s, 4 H), 8.9 (s, 4 H), 7.5 (d, 4 H), 7.4 (d, 4 H), 7.3 (s, 4 H), 1.5 (s, 36 H), 1.4 (s, 36 H). ^{13}C NMR (100 MHZ, CD_2Cl_2): δ 164.9, 158.8, 141.8, 140.8, 137.1, 128.6, 126.8, 118.5, 111.0, 35.4, 34.3, 31.3, 29,7. IR (KBr) (cm^{-1}): 2962, 2906, 2867, 1614, 1604, 1578, 1490, 1464, 1440, 1392, 1363, 1318, 1275, 1251, 1171, 1027, 981, 965, 939, 879, 873, 862, 831, 776, 748, 684, 643. Anal. Calcd for $C_{66}H_{90}N_4O_4$: C, 79.00; H, 9.04; N, 5.58. Found: C, 78.85; H, 9.01; N, 5.54.

Chromium(III)-salophen-chloride (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine)chromium(III)chloride ***C1****:*

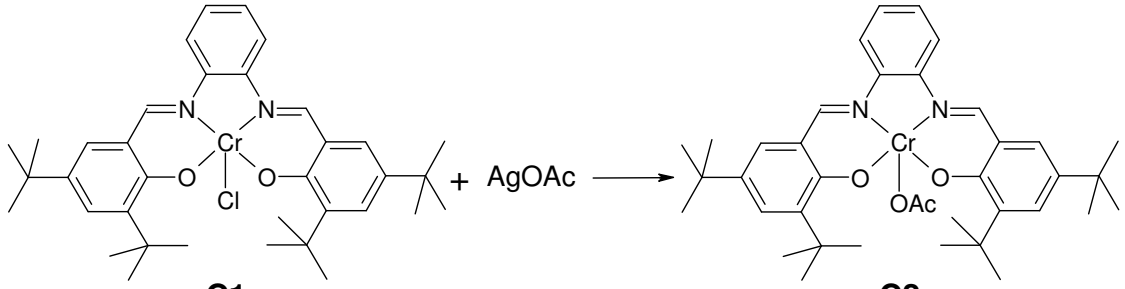


L2 **C1**

Tetra-*tert*-butyl-salophen **L2** (2.2 g, 4.0 mmol) and water free chromium(II) chloride (0.6 g, 5.0 mmol) were dissolved in anhydrous THF (80 ml) and stirred for 3 hours at room temperature, under argon. Afterwards, the flask was opened to air and the reaction mixture was stirred for additional 3 hours. The solution was then transferred into *tert*-butyl methyl ether (TBME) (400 ml), washed with saturated solution of brine (3 x 250 ml) and NH_4Cl (3 x 250 ml), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the resulting precipitate was dried under high vacuum to yield 2.1 g (84 %) as red solid.

IR (KBr) (cm^{-1}): 2955, 2903, 2866, 1604, 1578, 1526, 1483, 1461, 1424, 1387, 1359, 1328, 1298, 1254, 1197, 1171, 1132, 1105, 1080, 1025, 987, 958, 921, 871, 837, 784, 750, 636, 578, 559, 539, 490, 454. Anal. Calcd for $C_{36}H_{46}CrClN_2O_2$ * 1 THF: C, 68.80; H, 7.79; N, 4.01. Found: C, 68.82; H, 7.85; N, 3.99.

*Chromium(III)-salophen-acetate (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine)chromium(III)acetate **C2**:*

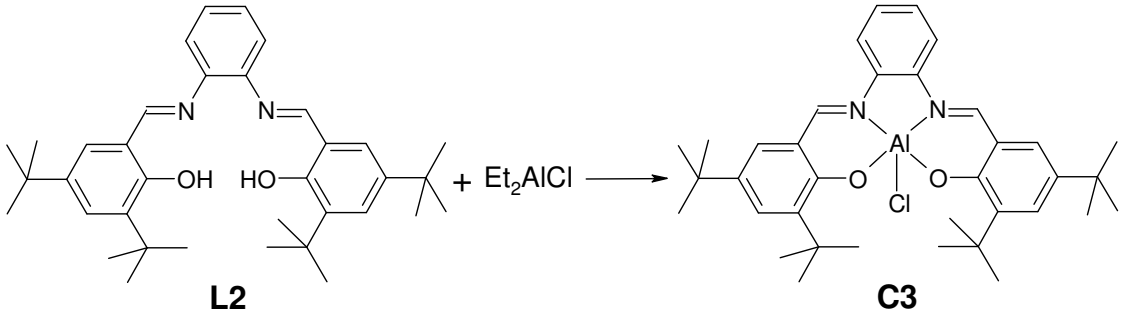


C1 **C2**

Chromium(III)-salophen-chloride **C1** (1.25 g, 2.0 mmol) was dissolved in anhydrous THF (40 ml). Silver acetate (0.5 g, 3.0 mmol) was added and the solution was stirred for 12 hours at room temperature. The solvent was removed under reduced pressure and the resulting precipitate was dissolved in a mixture of THF, CH_2Cl_2, TBME (ratio 1:1:8). The insoluble silver salts were filtered off (0.2 µm) and the solvents were removed under reduced pressure. The product was dried under high vacuum to yield 1.0 g (77 %) as dark red solid.

IR (KBr) (cm^{-1}): 2956, 2905, 2867, 1608, 1579, 1524, 1483, 1460, 1427, 1387, 1359, 1328, 1298, 1255, 1197, 1169, 1132, 1106, 1082, 1022, 956, 928, 869, 836, 814, 785, 747, 668, 637, 562, 536, 491, 453. Anal. Calcd for $C_{38}H_{49}CrN_2O_4$ * 0.5 THF: C, 70.05; H, 7.79; N, 4.08. Found: C, 70.25; H, 8.02; N, 4.08.

*Aluminium(III)-salophen-chloride (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine)aluminium(III)chloride **C3**:*

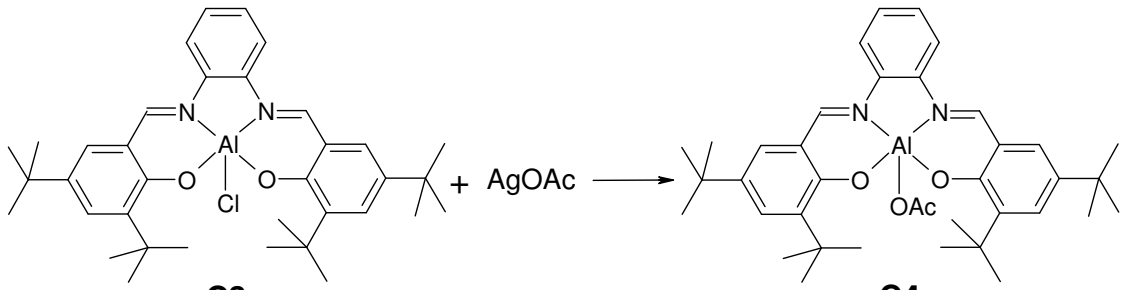


L2 **C3**

Tetra-*tert*-butyl-salophen **L2** (2.9 g, 5.3 mmol) was dissolved in anhydrous toluene (75 ml). After cooling the solution in an ice bath to 0°C, 5.3 ml of diethyl aluminium chloride (1.0 M solution in heptane, 5.3 mmol) were added slowly to the stirring solution. After removing the ice bath, the solution was stirred for 4 hours at ambient temperature. Afterwards, the solvents were removed under reduced pressure and the resulting precipitate was rinsed with anhydrous hexane (40 ml). The product was dried under high vacuum to yield 2.5 g (78 %) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.9 (s, 2 H), 7.8 (m, 2 H), 7.6 (d, 2 H), 7.4 (m, 2 H), 7.2 (d, 2 H), 1.6 (s, 18 H), 1.3 (s, 18 H). IR (KBr) (cm^{-1}): 3387, 2953, 2866, 1615, 1584, 1537, 1468, 1441, 1411, 1387, 1358, 1316, 1255, 1201, 1181, 1134, 1026, 985, 968, 927, 876, 846, 816, 785, 743, 639, 596, 569, 508, 444. Anal. Calcd for $C_{36}H_{46}AlClN_2O_2$: C, 71.92; H, 7.71; N, 4.66. Found: C, 71.84; H, 7.67; N, 4.64.

*Aluminium(III)-salophen-acetate (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine)aluminium(III)acetate **C4**:*

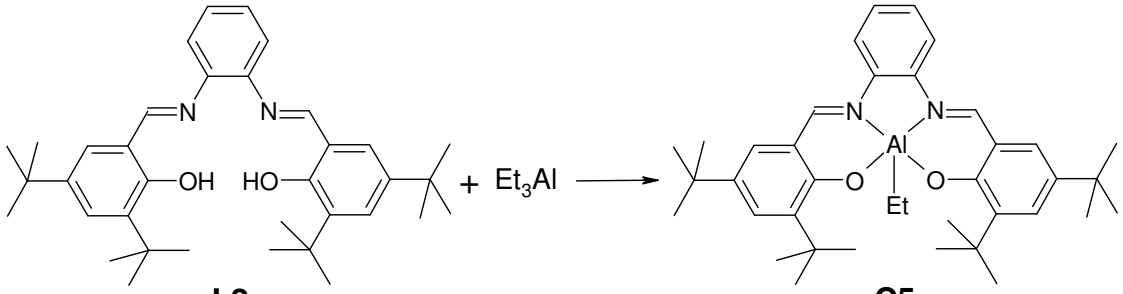


C3 **C4**

Aluminium(III)-salophen-chloride **C3** (1.9 g, 3.2 mmol) was dissolved in anhydrous toluene (40 ml). Silver acetate (0.6 g, 3.5 mmol) was added and the solution was stirred for 17 hours at room temperature. The insoluble silver salts were filtered off (0.2 µm) and the solvent was removed under reduced pressure. The product was dried under high vacuum to yield 1.2 g (60 %) as orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.9 (s, 2 H), 7.7 (m, 3 H), 7.6 (d, 2 H), 7.3 (m, 2 H), 7.2 (s, 2 H), 7.1 (d, 2 H), 1.4 (s, 18 H), 1.2 (s, 18 H). IR (KBr) (cm^{-1}): 3426, 2956, 2867, 1617, 1583, 1535, 1470, 1412, 1388, 1358, 1323, 1261, 1199, 1176, 1134, 1110, 1025, 967, 927, 871, 844, 813, 787, 749, 657, 595, 550, 469, 464. Anal. Calcd for $C_{38}H_{49}AlN_2O_4$: C, 73.05; H, 7.90; N, 4.48. Found: C, 71.29; H, 7.84; N, 4.31.

*Aluminium(III)-salophen-ethyl (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine)aluminium(III)ethyl **C5**:*

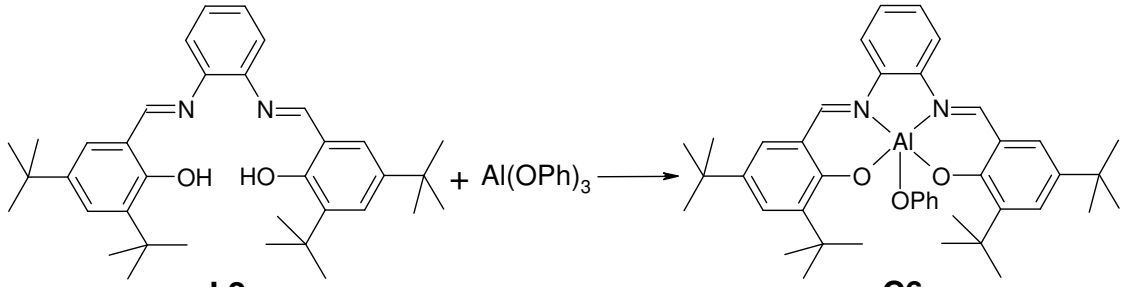


L2 **C5**

Tetra-*tert*-butyl-salophen **L2** (10.0 g, 18.5 mmol) was dissolved in anhydrous toluene (50 ml). After cooling the solution in an ice bath to 0°C, 18.5 ml of triethyl aluminium (1.0 M solution in hexane, 18.5 mmol) were added slowly to the stirring solution. After removing the ice bath, the solution was stirred for 4 hours at ambient temperature. Afterwards, the solvents were removed under reduced pressure and the resulting precipitate was rinsed with anhydrous hexane (60 ml). The product was dried under high vacuum to yield 8.3 g (76 %) as orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.8 (s, 2 H), 7.7 (m, 2 H), 7.6 (d, 2 H), 7.4 (m, 2 H), 7.2 (m, 2 H), 1.6 (s, 18 H), 1.4 (s, 18 H), 0.6 (t, 3 H), -0.4 (q, 2 H). IR (KBr) (cm^{-1}): 2958, 2935, 2901, 1614, 1583, 1535, 1469, 1384, 1359, 1261, 1201, 1178, 1095, 1026, 869, 841, 750, 607, 580. Anal. Calcd for $C_{38}H_{51}AlN_2O_2$: C, 76.73; H, 8.64; N, 4.71. Found: C, 76.39; H, 8.66; N, 4.66. MS (MALDI, matrix: anthralin): *m/z* = 565 $[M - Et]^+$.

*Aluminium(III)-salophen-phenoxide (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine)aluminium(III)phenoxide **C6**:*

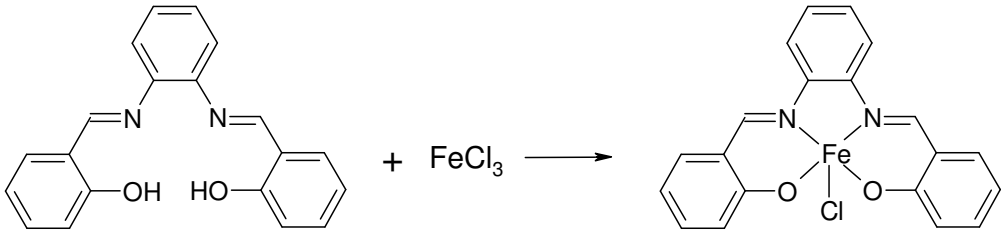


L2 **C6**

Tetra-*tert*-butyl-salophen **L2** (1.35 g, 2.5 mmol) and triphenoxy aluminium (0.77 g, 2.5 mmol) were dissolved in anhydrous toluene (30 ml) and heated under reflux for 3 hours. Afterwards, the solvents were removed under reduced pressure and the resulting precipitate was rinsed with anhydrous hexane (30 ml). The product was dried under high vacuum to yield 1.2 g (73 %) as yellow solid.

^{1}H NMR (400 MHz, C_6D_6): δ 7.8 (m, 2 H), 7.5 (s, 2 H), 7.0 (m, 2 H), 6.8 (m, 2 H), 6.7 (m, 2 H), 3.2 (m, 2 H), 2.6 (m, 2 H), 1.8 (s, 18 H), 1.4 (s, 18 H). IR (KBr) (cm^{-1}): 3425, 2954, 2866, 1617, 1586, 1536, 1469, 1440, 1413, 1388, 1359, 1317, 1256, 1199, 1167, 1067, 1024, 996, 971, 928, 870, 844, 814, 786, 753, 690, 664, 590, 566, 507, 428. Anal. Calcd for $C_{42}H_{51}AlN_2O_3$: C, 76.57; H, 7.80; N, 4.25. Found: C, 76.04; H, 7.81; N, 3.99. MS (MALDI, matrix: anthralin): *m/z* = 565 $[M - OPh]^+$.

Iron(III)-salophen-chloride (salicylidene-1,2-phenylene diimine)iron(III)chloride ***C7****:*

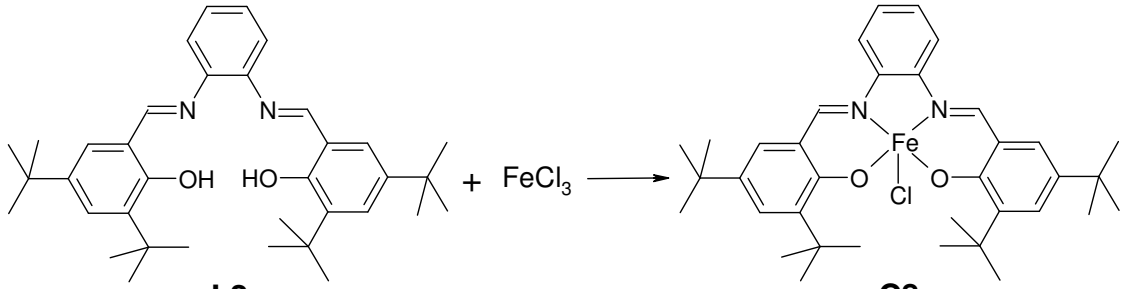


L1 **C7**

Salophen **L1** (2.2 g, 7.0 mmol) was dissolved in dehydrated ethanol (100 ml). A solution of anhydrous iron(III) chloride (1.25 g, 7.7 mmol) in ethanol (30 ml) was added slowly. The solution was stirred for 18 hours, filtrated and the obtained precipitate was washed with diethyl ether (3 x 30 ml). The product was dried under high vacuum to yield 1.9 g (68 %) as black solid.

IR (KBr) (cm^{-1}): 2967, 2926, 1604, 1578, 1534, 1462, 1439, 1378, 1313, 1197, 1148, 1124, 924, 870, 812, 759, 614, 537. Anal. Calcd for $C_{20}H_{14}ClFeN_2O_2$ * 1 C_2H_6O: C, 58.84; H, 4.00; N, 6.53. Found: C, 57.33; H, 4.06; N, 6.45.

*Iron(III)-salophen-chloride (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine)iron(III)chloride **C8**:*

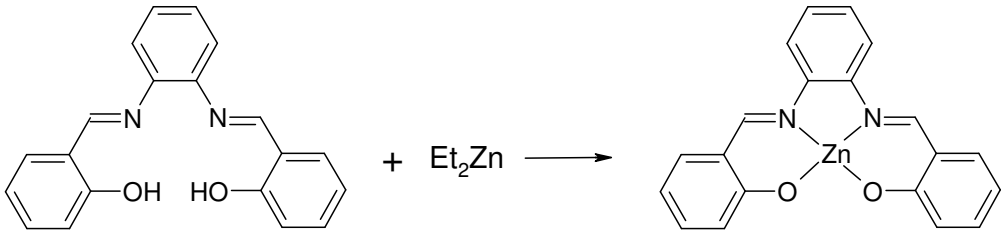


L2 **C8**

Tetra-*tert*-butyl-salophen **L2** (3.8 g, 7.0 mmol) was dissolved in dehydrated ethanol (130 ml). A solution of anhydrous iron(III) chloride (1.25 g, 7.7 mmol) in ethanol (30 ml) was added slowly. The solution was stirred for 18 hours, filtrated and the obtained precipitate was washed with diethyl ether (3 x 30 ml). The product was dried under high vacuum to yield 3.0 g (68 %) as black solid.

IR (KBr) (cm^{-1}): 2955, 2900, 2865, 1606, 1597, 1576, 1530, 1485, 1460, 1422, 1385, 1357, 1315, 1271, 1250, 1197, 1178, 1134, 1105, 840, 780, 745, 558, 542. Anal. Calcd for $C_{36}H_{46}ClFeN_2O_2$: C, 68.63; H, 7.36; N, 4.45. Found: C, 68.14; H, 7.37; N, 4.44.

Zinc(II)-salophen (salicylidene-1,2-phenylene diimine)zinc(II) ***C9****:*

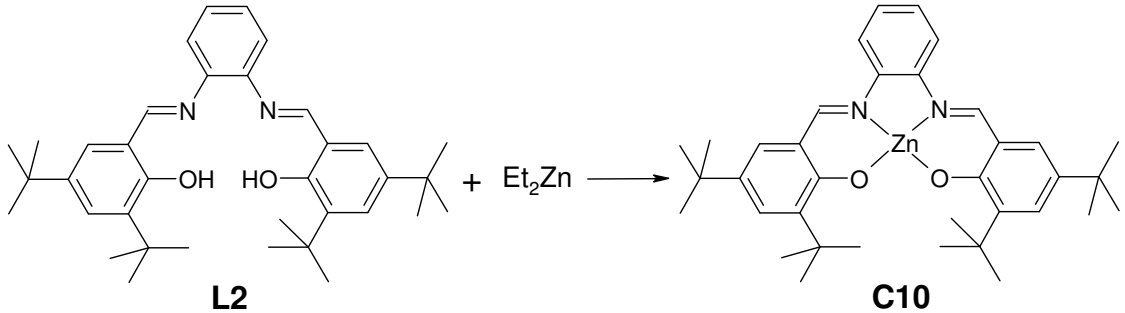


L1 **C9**

Salophen **L1** (0.95 g, 3.0 mmol) was dissolved in anhydrous THF (100 ml). After cooling the solution in an ice bath to 0℃, 3.0 ml of diethyl zinc (1.1 M solution in toluene, 3.3 mmol) were added slowly to the stirring solution. After removing the ice bath, the solution was stirred for 2 hours at ambient temperature. Afterwards, the solvents were removed under reduced pressure and the obtained product was dried under high vacuum to yield 0.9 g (82 %) as yellow solid.

IR (KBr) (cm^{-1}): 3049, 3013, 2967, 2856, 1611, 1584, 1543, 1525, 1462, 1441, 1386, 1331, 1292, 1247, 1179, 1145, 1123, 972, 917, 843, 795, 742, 601, 532, 510, 490, 437. Anal. Calcd for $C_{20}H_{14}N_2O_2Zn$: C, 63.26; H, 3.72; N, 7.38. Found: C, 62.42; H, 3.56; N, 7.45.

Zinc(II)-salophen (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine) zinc(II) ***C10****:*

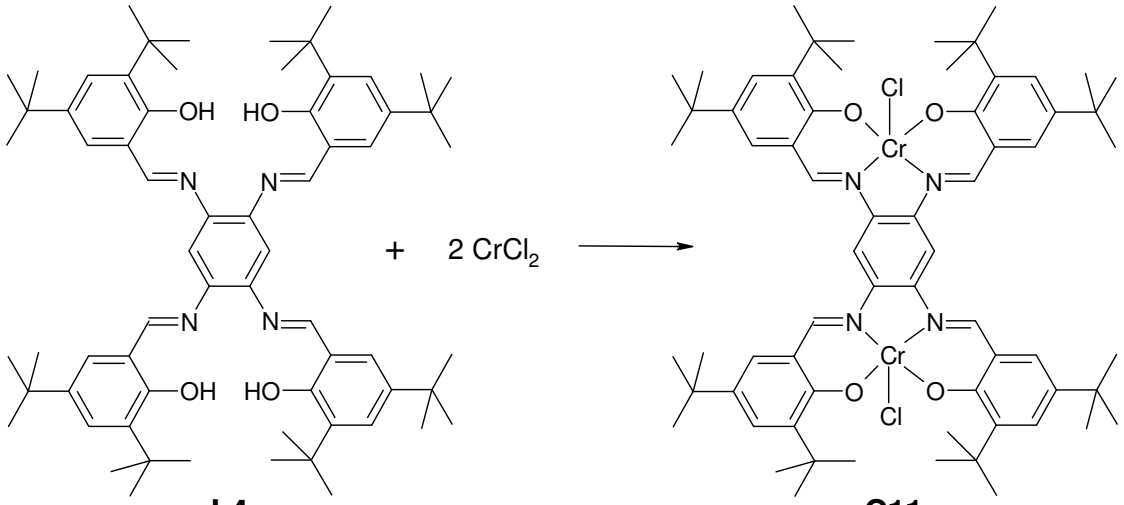


L2 **C10**

Tetra-*tert*-butyl-salophen **L2** (2.4 g, 4.5 mmol) was dissolved in anhydrous THF (150 ml). After cooling the solution in an ice bath to 0°C, 4.5 ml of diethyl zinc (1.1 M solution in toluene, 5.0 mmol) were added slowly to the stirring solution. After removing the ice bath, the solution was stirred for 2 hours at ambient temperature. Afterwards, the solvents were removed under reduced pressure and the obtained product was dried under high vacuum to yield 2.3 g (85 %) as orange solid.

IR (KBr) (cm^{-1}): 2951, 2899, 2865, 1614, 1602, 1582, 1546, 1523, 1465, 1439, 1406, 1385, 1357, 1336, 1293, 1254, 1195, 1167, 1130, 1111, 1040, 966, 915, 872, 833, 792, 747, 634, 524, 493. Anal. Calcd for $C_{36}H_{46}N_2O_2Zn$ * 1 THF: C, 71.04; H, 8.05; N, 4.14. Found: C, 69.03; H, 7.89; N, 3.95.

(Bis-salophen)(CrCl)$_2$ (N',N'',N''',N''''-tetra-(3,5-di-tert-butylsalicylidene)-1,2,4,5-phenylene tetraimine)-di-chromium(III)chloride ***C11****:*

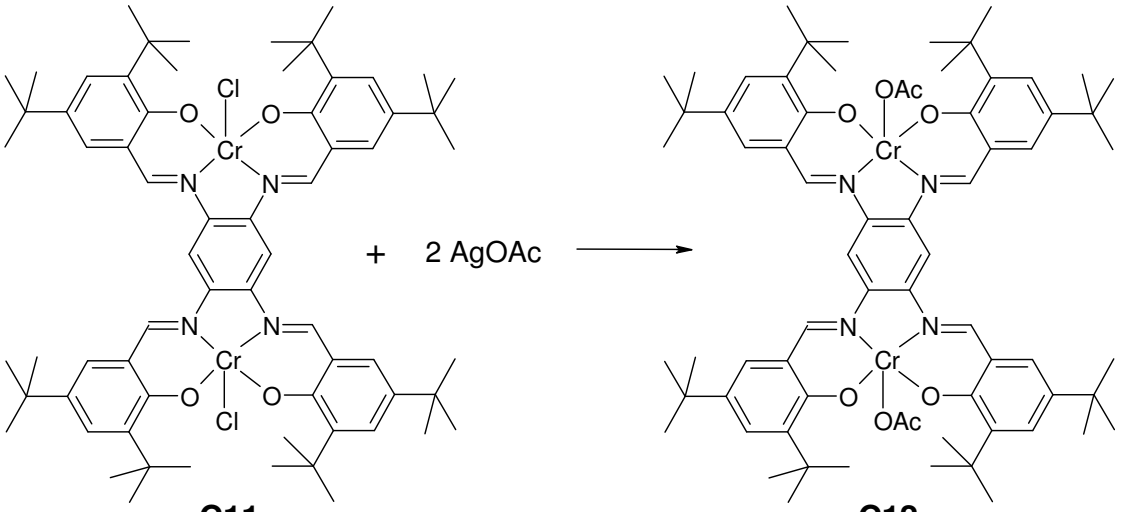


L4 **C11**

Bis-salophen **L4** (1.0 g, 1.0 mmol) and water free chromium(II) chloride (0.27 g, 2.2 mmol) were dissolved in anhydrous THF (20 ml). The solution was heated under reflux for 4 hours. After cooling to room temperature, the flask was opened to air and the reaction mixture was stirred for additional 12 hours. The solution was then transferred into *tert*-butyl methyl ether (TBME) (200 ml), washed with saturated solution of brine (3 x 100 ml) and NH_4Cl (3 x 100 ml), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the resulting precipitate was dried under high vacuum to yield 1.1 g (91 %) as dark red solid.

IR (KBr) (cm^{-1}): 2955, 2904, 2867, 1610, 1583, 1550, 1526, 1494, 1461, 1417, 1383, 1359, 1323, 1293, 1254, 1238, 1168, 1132, 1095, 1026, 987, 950, 930, 911, 882, 861, 848, 821, 802, 784, 746, 692, 662, 634, 559, 542, 498, 456. Anal. Calcd for $C_{66}H_{86}Cl_2Cr_2N_4O_4$ * 2 THF: C, 67.41; H, 7.80; N, 4.25. Found: C, 67.73; H, 7.77; N, 4.32. MS (MALDI, matrix: anthralin): *m/z* = 1103 $[M - 2 \times Cl]^+$.

(Bis-salophen)(CrOAc)$_2$ (N',N'',N''',N''''-tetra-(3,5-di-tert-butylsalicylidene)-1,2,4,5-phenylene tetraimine)-di-chromium(III)acetate ***C12****:*

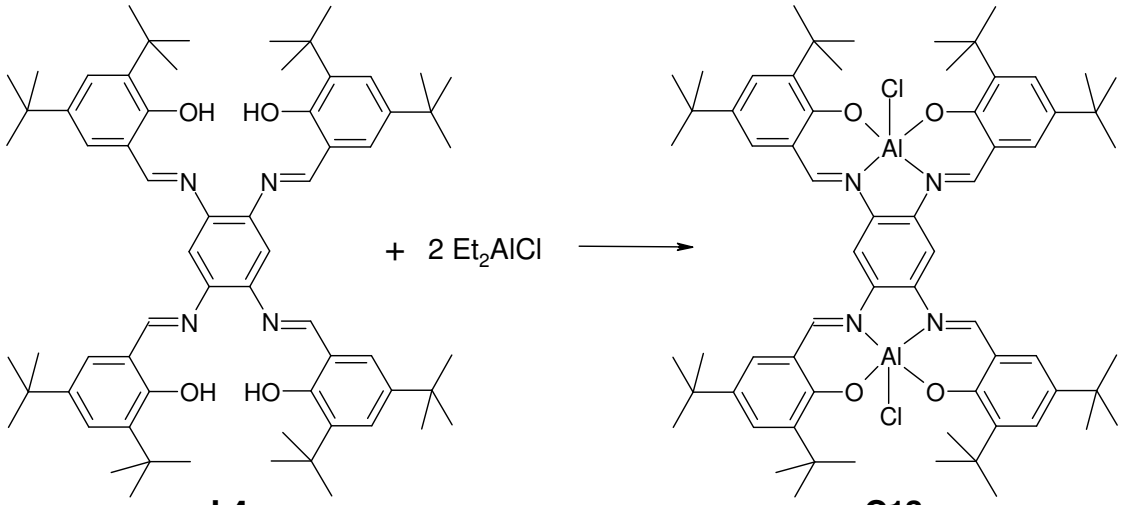


C11 **C12**

(Bis-salophen)(CrCl)$_2$ **C11** (1.2 g, 1.0 mmol) was dissolved in anhydrous CH_2Cl_2 (7.5 ml) and anhydrous THF (2.5 ml). Silver acetate (0.5 g, 3.0 mmol) was added and the solution was stirred for 18 hours at room temperature. The solvents were removed under reduced pressure and the resulting precipitate was dissolved in 40 ml of a mixture of THF, CH_2Cl_2, TBME (ratio 1:1:8). The insoluble silver salts were filtered off (0.2 µm) and the solvents were removed under reduced pressure. The product was dried under high vacuum to yield 0.9 g (73 %) as claret-red solid.

IR (KBr) (cm^{-1}): 2957, 2913, 2869, 1612, 1586, 1526, 1461, 1420, 1385, 1360, 1320, 1253, 1233, 1195, 1166, 1132, 1023, 950, 912, 875, 844, 783, 747, 665, 542, 491, 416. Anal. Calcd for $C_{70}H_{92}Cr_2N_4O_8$ * 2 THF: C, 68.60; H, 7.97; N, 4.10. Found: C, 68.30; H, 7.95; N, 4.02. MS (MALDI, matrix: anthralin): *m/z* = 1103 $[M - 2 \times OAc]^+$.

*(Bis-salophen)(AlCl)$_2$ (N',N'',N''',N''''-tetra-(3,5-di-tert-butylsalicylidene)-1,2,4,5-phenylene tetraimine)-di-aluminium(III)chloride **C13**:*

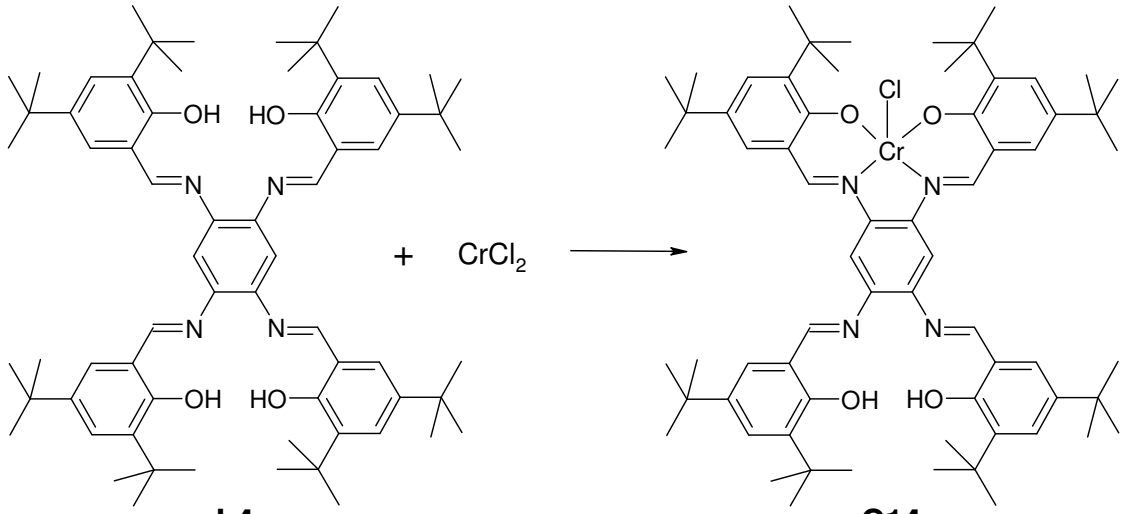


L4 **C13**

Bis-salophen **L4** (0.9 g, 0.9 mmol) was dissolved in anhydrous THF (20 ml). After cooling the solution to 0°C, 1.1 ml of diethyl aluminium chloride (1.8 M solution in hexane, 2.0 mmol) were added slowly to the stirring solution. After removing the ice bath, the solution was heated under reflux for 15 hours. Afterwards, the solvents were removed under reduced pressure and the resulting precipitate was rinsed with anhydrous hexane (10 ml). The product was dried under high vacuum to yield 0.95 g (94 %) as brick-red solid.

IR (KBr) (cm^{-1}): 2956, 2912, 2873, 1614, 1591, 1539, 1502, 1467, 1439, 1412, 1388, 1361, 1313, 1256, 1179, 1134, 1106, 1031, 991, 918, 882, 852, 786, 756, 604, 501, 439. Anal. Calcd for $C_{66}H_{86}Al_2Cl_2N_4O_4$: C, 70.51; H, 7.71; N, 4.98. Found: C, 67.64; H, 7.82; N, 4.87. MS (MALDI, matrix: anthralin): *m/z* = 1124 $[M]^+$.

(Bis-salophen)(CrCl) (N',N'',N''',N''''-tetra-(3,5-di-tert-butylsalicylidene)-1,2,4,5-phenylene tetraimine)chromium(III)chloride ***C14****:*

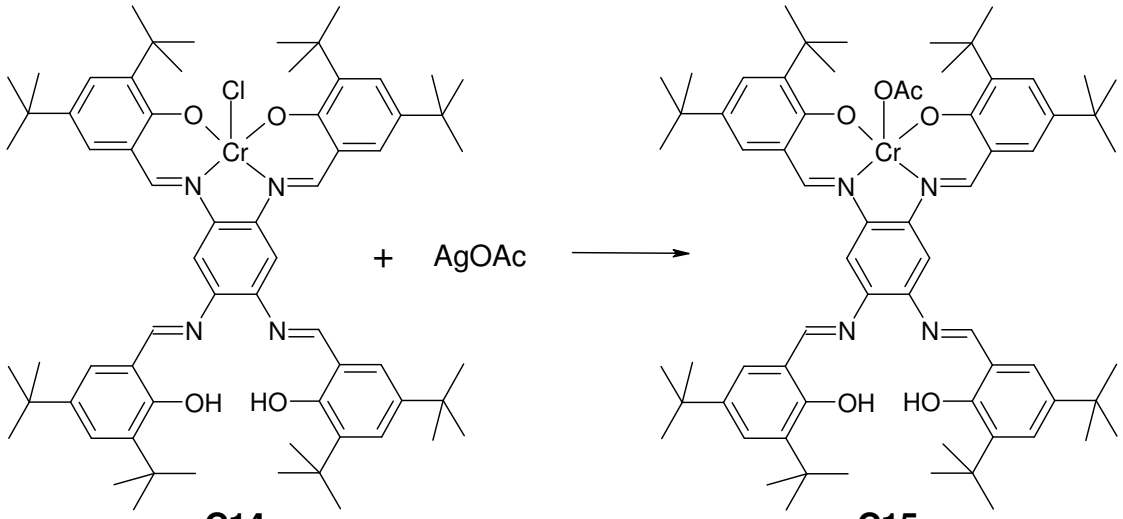


L4 **C14**

Bis-salophen **L4** (1.8 g, 1.8 mmol) and water free chromium(II) chloride (0.22 g, 1.8 mmol) were dissolved in anhydrous THF (30 ml). The solution was heated under reflux for 4 hours. After cooling to room temperature, the flask was opened to air and the reaction mixture was stirred for additional 12 hours. The solvent was removed under reduced pressure and the resulting precipitate was purified by column chromatography (mixture of hexane and THF, ratio 9:1). The product was dried under high vacuum to yield 1.4 g (72 %) red solid.

IR (KBr) (cm^{-1}): 2955, 2904, 2867, 1610, 1584, 1527, 1494, 1461, 1418, 1384, 1359, 1322, 1294, 1253, 1237, 1169, 1132, 1027, 985, 950, 911, 882, 860, 802, 783, 746, 693, 662, 635, 542, 497. Anal. Calcd for $C_{66}H_{88}ClCrN_4O_4$ * 1 THF: C, 72.42; H, 8.33; N, 4.83. Found: C, 72.08; H, 8.38 N, 4.74. MS (MALDI, matrix: anthralin): m/z = 1053 $[M\text{-}Cl]^+$.

(Bis-salophen)(CrOAc) (N',N'',N''',N''''-tetra-(3,5-di-tert-butylsalicylidene)-1,2,4,5-phenylene tetraimine)chromium(III)acetate ***C15****:*

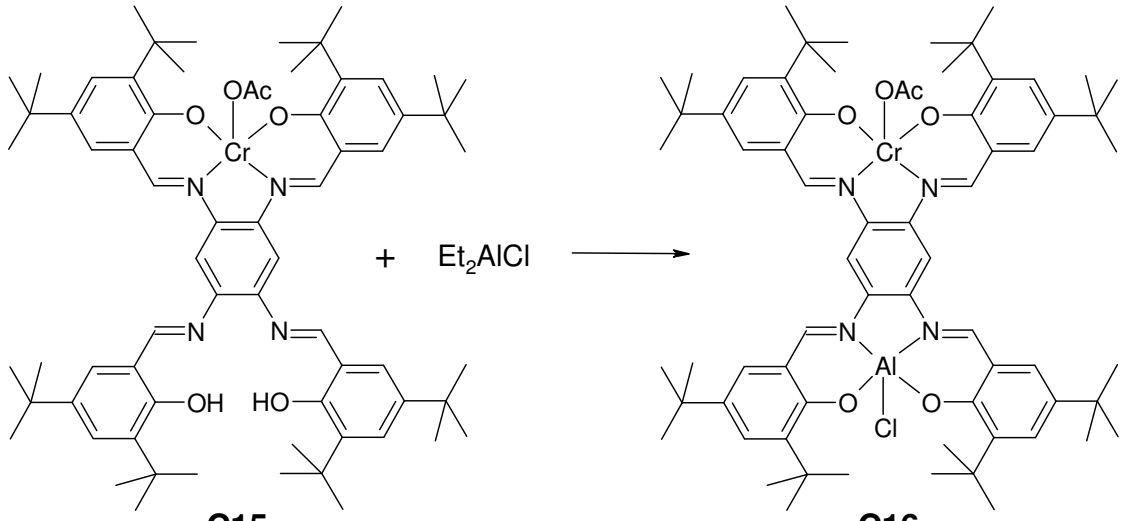


C14 **C15**

(Bis-salophen)(CrCl) **C14** (1.2 g, 1.0 mmol) was dissolved in anhydrous CH_2Cl_2 (7.5 ml) and anhydrous THF (2.5 ml). Silver acetate (0.4 g, 2.2 mmol) was added and the solution was stirred for 18 hours at room temperature. The solvents were removed under reduced pressure and the resulting precipitate was dissolved in 40 ml of a mixture of THF, CH_2Cl_2, TBME (ratio 1:1:4). The insoluble silver salts were filtered off (0.2 µm) and the solvents were removed under reduced pressure. The product was dried under high vacuum to yield 1.1 g (92 %) as red solid.

IR (KBr) (cm^{-1}): 2956, 2907, 2868, 1724, 1610, 1587, 1526, 1461, 1422, 1385, 1360, 1321, 1253, 1233, 1195, 1166, 1133, 1023, 911, 876, 845, 784, 747, 666, 636, 542. Anal. Calcd for $C_{68}H_{91}CrN_4O_6$ * 1 THF: C, 73.00; H, 8.42; N, 4.73. Found: C, 72.23; H, 8.47; N, 4.64. MS (MALDI, matrix: anthralin): *m/z* = 1053 $[M - OAc]^+$.

(Bis-salophen)(CrOAc)(AlCl) (N',N'',N''',N''''-tetra-(3,5-di-tert-butylsalicylidene)-1,2,4, 5-phenylene tetraimine)(chromium(III)acetate)(aluminium(III)chloride) ***C16****:*

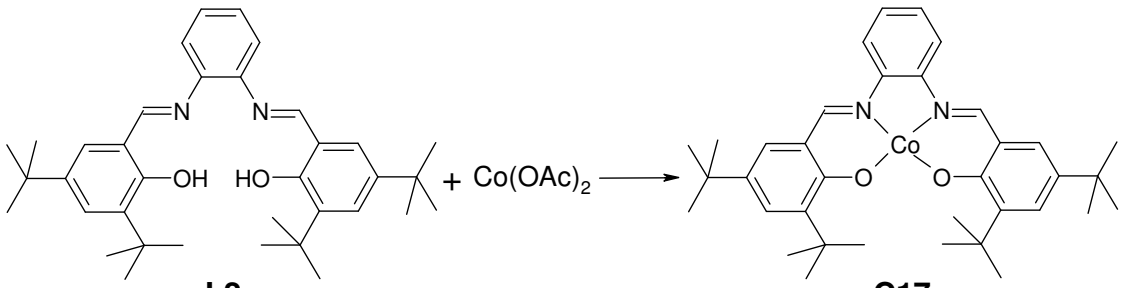


C15 **C16**

(Bis-salophen)(CrOAc) **C15** (1.1 g, 1.0 mmol) was dissolved in anhydrous THF (20 ml). After cooling the solution to 0 °C, 0.7 ml of diethyl aluminium chloride (1.8 M solution in hexane, 1.25 mmol) were added slowly to the stirring solution. After removing the ice bath, the solution was heated under reflux for 5 hours. Afterwards, the solvents were removed under reduced pressure and the resulting precipitate was rinsed with anhydrous hexane (10 ml). The product was dried under high vacuum to yield 0.8 g (70 %) as red solid.

IR (KBr) (cm^{-1}): 2955, 2906, 2867, 1608, 1586, 1526, 1460, 1420, 1385, 1360, 1252, 1196, 1167, 1132, 1023, 911, 876, 843, 784, 747, 667, 541. Anal. Calcd for $C_{68}H_{89}AlClCrN_4O_6$ * 1 THF: C, 69.46; H, 7.85; N, 4.50. Found: C, 68.92; H, 7.74; N, 4.56. MS (MALDI, matrix: anthralin): *m/z* = 1076 $[M - Cl - OAc]^+$.

Cobalt(II)-salophen (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine) cobalt(II) ***C17****:*

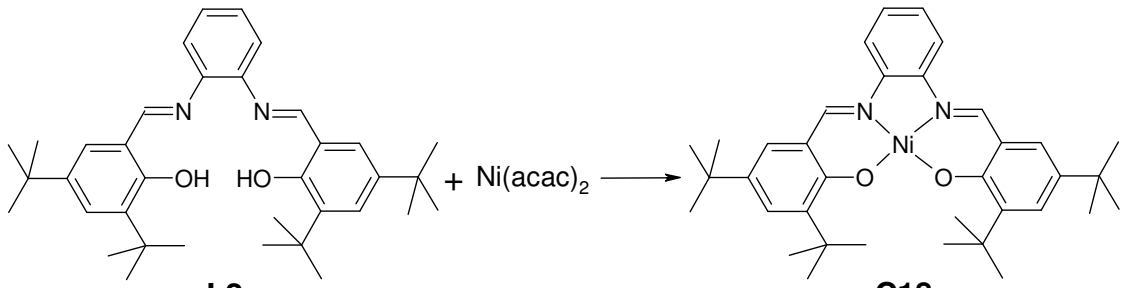


L2 **C17**

Tetra-*tert*-butyl-salophen **L2** (2.7 g, 5.0 mmol) and cobalt(II) acetate tetrahydrate (1.4 g, 5.6 mmol) were dissolved in anhydrous methanol (100 ml) and heated under reflux for 2 hours. The mixture was then cooled, filtered and the resulting precipitate was washed with cooled methanol. The product was dried under high vacuum to yield 2.4 g (80 %) as brown solid.

IR (KBr) (cm^{-1}): 2954, 2902, 2861, 1616, 1604, 1582, 1541, 1522, 1465, 1407, 1382, 1361, 1341, 1296, 1191, 1129, 1114, 1043, 967, 915, 870, 831, 795, 745, 632. Anal. Calcd for $C_{36}H_{46}CoN_2O_2$: C, 72.34; H, 7.76; N, 4.69. Found: C, 70.84; H, 7.84; N, 4.78.

Nickel(II)-salophen (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine) nickel(II) ***C18****:*

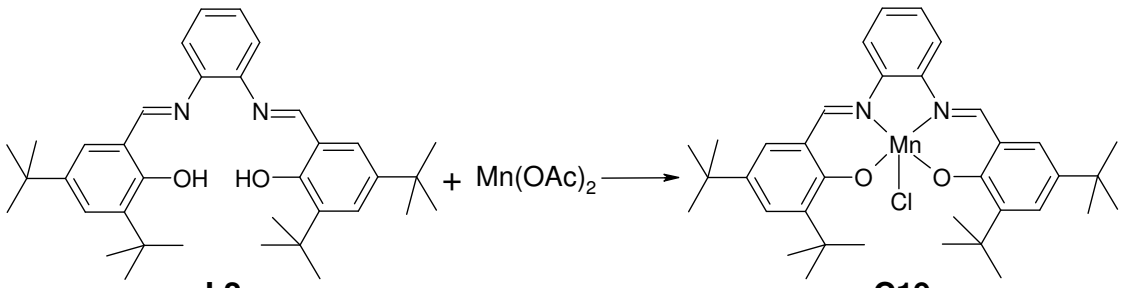


L2 **C18**

Tetra-*tert*-butyl-salophen **L2** (1.0 g, 1.9 mmol) and nickel(II) acetylacetonate hydrate (0.5 g, 2.0 mmol) were dissolved in anhydrous ethanol (70 ml) and heated under reflux for 2 hours. The mixture was cooled, filtered and the resulting precipitate was washed with cooled ethanol. The product was dried under high vacuum to yield 1.1 g (92 %) as red solid.

IR (KBr) (cm^{-1}): 2955, 2904, 2865, 1609, 1578, 1543, 1523, 1488, 1463, 1427, 1386, 1358, 1329, 1265, 1244, 1198, 1177, 1129, 1045, 1025, 936, 918, 886, 867, 832, 784, 738, 635, 590, 565, 537, 419. Anal. Calcd for $C_{36}H_{46}N_2NiO_2$: C, 72.37; H, 7.76; N, 4.69. Found: C, 72.42; H, 7.81; N, 4.51. MS (MALDI, matrix: anthralin): $m/z = 597$ $[M]^+$.

Manganese(III)-salophen-chloride (N,N'-bis-(3,5-di-tert-butylsalicylidene)-1,2-phenylene diimine)manganese(III)chloride ***C19****:*

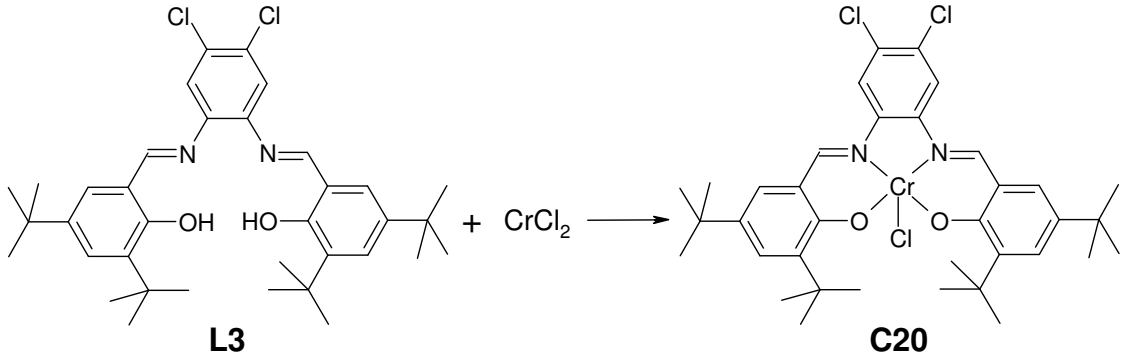


L2 **C19**

Tetra-*tert*-butyl-salophen **L2** (1.0 g, 1.9 mmol) and manganese(II) acetate tetrahydrate (0.6 g, 2.4 mmol) were dissolved in anhydrous ethanol (70 ml) and heated under reflux for 3 hours. After cooling to room temperature, the flask was opened to air and the reaction mixture was stirred for additional 1 hour. After adding a saturated solution of sodium chloride (25 ml) the reaction mixture was heated again under reflux for 3 hours. The mixture was filtered and the solvent was removed under reduced pressure. The resulting precipitate was dissolved in CH_2Cl_2 (100 ml). The solution then was transferred into *tert*-butyl methyl ether (TBME) (100 ml), washed with saturated solution of brine (3 x 150 ml) and NH_4Cl (3 x 150 ml), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the product was dried under high vacuum to yield 1.2 g (67 %) as brown solid.

IR (KBr) (cm^{-1}): 2957, 2907, 2868, 1611, 1598, 1576, 1529, 1486, 1463, 1421, 1388, 1359, 1315, 1250, 1198, 1179, 1133, 1026, 959, 924, 871, 837, 810, 780, 749, 637, 562, 540, 490. Anal. Calcd for $C_{36}H_{46}ClMnN_2O_2$: C, 68.73; H, 7.37; N, 4.45. Found: C, 66.82; H, 7.35; N, 4.12. MS (MALDI, matrix: anthralin): *m/z* = 593 $[M - Cl]^+$.

*Chromium(III)-dichloro-salophen-chloride (N,N'-bis-(3,5-di-tert-butylsalicylidene)-4,5-dichloro-1,2-phenylene diimine)chromium(III)chloride **C20**:*

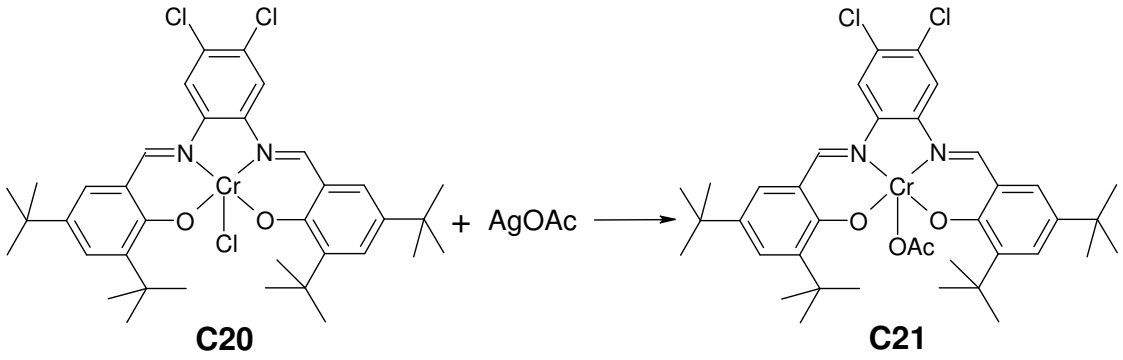


L3 **C20**

Tetra-*tert*-butyl-dichloro-salophen **L3** (1.5 g, 2.5 mmol) and water free chromium(II) chloride (0.35 g, 2.85 mmol) were dissolved in anhydrous THF (60 ml) and stirred for 3 hours at room temperature, under argon. Afterwards, the flask was opened to air and the reaction mixture was stirred for additional 3 hours. The solution was transferred into *tert*-butyl methyl ether (TBME) (250 ml), washed with saturated solution of brine (3 x 150 ml) and NH_4Cl (3 x 150 ml), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the resulting precipitate was dried under high vacuum to yield 1.4 g (80 %) as red solid.

IR (KBr) (cm^{-1}): 2954, 2907, 2864, 1617, 1598, 1522, 1464, 1423, 1384, 1356, 1258, 1225, 1198, 1173, 1125, 1082, 957, 927, 886, 864, 838, 784, 747, 682, 634, 578, 539, 483, 417.Anal. Calcd for $C_{36}H_{44}CrCl_3N_2O_2$: C, 62.21; H, 6.38; N, 4.03. Found: C, 60.84; H, 6.54; N, 3.96.

*Chromium(III)-dichloro-salophen-acetate (N,N'-bis-(3,5-di-tert-butylsalicylidene)-4,5-dichloro-1,2-phenylene diimine)chromium(III)acetate **C21**:*

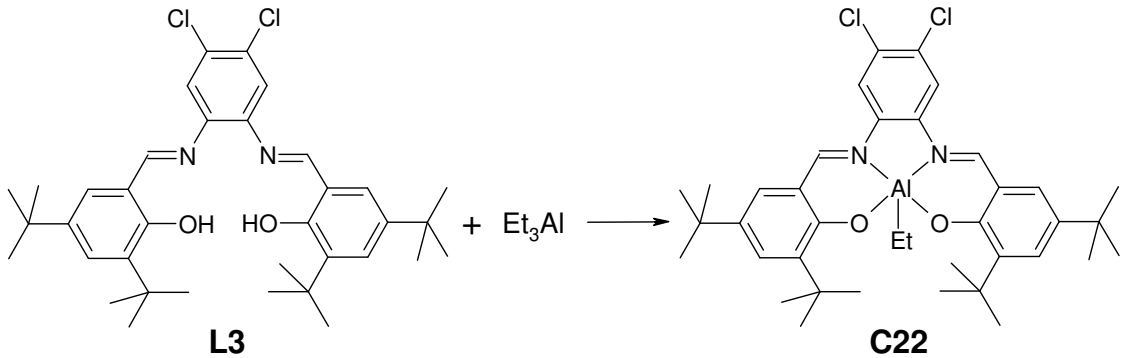


C20 **C21**

Chromium(III)-dichloro-salophen-chloride **C20** (1.0 g, 1.4 mmol) was dissolved in anhydrous THF (30 ml). Silver acetate (0.4 g, 2.4 mmol) was added and the solution was stirred for 17 hours at room temperature. The solvent was removed under reduced pressure and the resulting precipitate was dissolved in a mixture of THF, CH_2Cl_2, TBME (ratio 1:1:8). The insoluble silver salts were filtered off (0.2 µm) and the solvents were removed under reduced pressure. The product was dried under high vacuum to yield 0.84 g (83 %) as dark red solid.

IR (KBr) (cm^{-1}): 2956, 2905, 2867, 1621, 1596, 1522, 1462, 1423, 1388, 1358, 1256, 1227, 1197, 1171, 1126, 1082, 953, 929, 888, 863, 839, 784, 749, 680, 634, 577, 538, 480, 414. Anal. Calcd for $C_{38}H_{47}CrCl_2N_2O_4$: C, 63.51; H, 6.59; N, 3.90. Found: C, 62.67; H, 6.95; N, 3.65

*Aluminium(III)-dichloro-salophen-ethyl (N,N'-bis-(3,5-di-tert-butylsalicylidene)-4,5-dichloro-1,2-phenylene diimine)aluminium(III)ethyl **C22**:*



L3 **C22**

Tetra-*tert*-butyl-dichloro-salophen **L3** (3.0 g, 5.0 mmol) was dissolved in anhydrous toluene (25 ml). After cooling the solution in an ice bath to 0 °C, 5.0 ml of triethyl aluminium (1.0 M solution in hexane, 5.0 mmol) were added slowly to the stirring solution. After removing the ice bath, the solution was stirred for 3 hours at ambient temperature. Afterwards, the solvents were removed under reduced pressure and the resulting precipitate was rinsed with anhydrous hexane (25 ml). The product was dried under high vacuum to yield 2.5 g (75 %) as dark red solid.

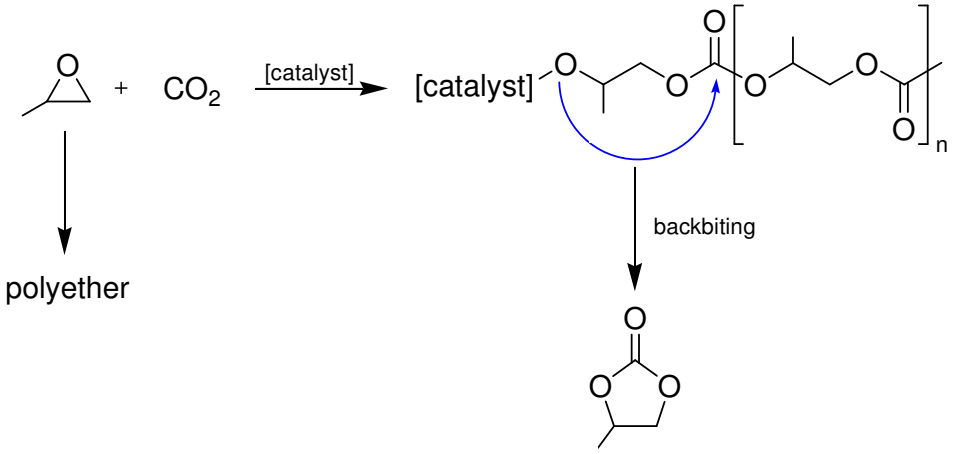
IR (KBr) (cm^{-1}): 2956, 2903, 2866, 1617, 1578, 1533, 1468, 1440, 1415, 1389, 1357, 1328, 1259, 1230, 1201, 1178, 1154, 1130, 1026, 968, 928, 893, 867, 843, 787, 753, 681, 598, 555, 475, 414. Anal. Calcd for $C_{38}H_{49}AlCl_2N_2O_2$: C, 68.77; H, 7.44; N, 4.22. Found: C, 64.46; H, 7.21; N, 4.01.

5.3 REFERENCES

[1] B. Cornils, W. A. Herrmann, *"Applied Homogeneous Catalysis with Organometallic Compounds"*, 1st edition, VCH Publishers, New York, **1996**.

SUMMARY

The huge majority of synthetic polymers base on crude oil as feedstock. Because of the non-renewable nature of these materials, there is increasing interest in developing sustainable routes to polymeric materials from renewable resources. In addition, there is a growing need for polymeric materials that can be eliminated through biodegradation. Aliphatic polycarbonates out of carbon dioxide and propylene oxide have the potential to achieve these important goals (Scheme 1).



Scheme 1 **Copolymerisation reaction of propylene oxide and CO_2. Formation of two possible by-products (polyether and cyclic carbonate).**

Over the last decade, significant advances have been achieved in epoxide-CO_2 coupling chemistry. In contrast to their heterogeneous counterparts, homogeneous catalysts offer significant increases in overall consumption as well as selectivity for the copolymerisation of epoxides and carbon dioxide. Well defined, homogeneous catalysts give various new impulses to the field of CO_2 utilisation and lead to a much deeper mechanistic understanding of these systems. Present catalysts provide practical routes to a variety of polycarbonates

from inexpensive epoxides (e.g. propylene oxide), including poly(propylene carbonate), poly(cyclohexene carbonate) and terpolymers of PO, CHO and CO_2. Moreover, catalyst systems were found that generate block copolymers with molecular weights predetermined by monomer/initiator ratios. In addition, both polycarbonates and cyclic carbonates can be synthesised with high selectivities and rates as a result of insignificant modifications of the catalyst's architecture. Finally, systematic control of polycarbonate and/or cyclic carbonate formation is achieved by the use of homogeneous catalysts with convenient reaction conditions (co-catalyst, concentrations, temperature and pressure).

The present work shows, that the copolymerisation of PO and CO_2 mediated by metal-salophen/nucleophile systems has a complex dependence on the concentration and ratios of all components. In the bimetallic system with chromium(III)-salophen-acetate and aluminium(III)-salophen-chloride as catalyst, there is a maximum selectivity for the aliphatic poly(propylene carbonate) (PPC) at about 14 bar of CO_2 pressure, 75°C, 3000 equivalents propylene oxide and 0.5 equivalents co-catalyst (NBu_4Cl). The parabolic dependence on the selectivity for PPC formation and PO conversion on the concentration of nucleophile is consistent with a bimolecular chain growth in which a metal-bound carbonate attacks an activated (coordinated) epoxide (Figure 1).

Remarkable, systems with exclusively aluminium(III)-salophen complexes as catalysts result only in cyclic carbonate as product. Models are proposed that account for the differences in catalytic action and include anion dissociation as the rate-determining step in case of chromium(III)-salophen and CO_2 insertion for aluminium(III)-salophen.

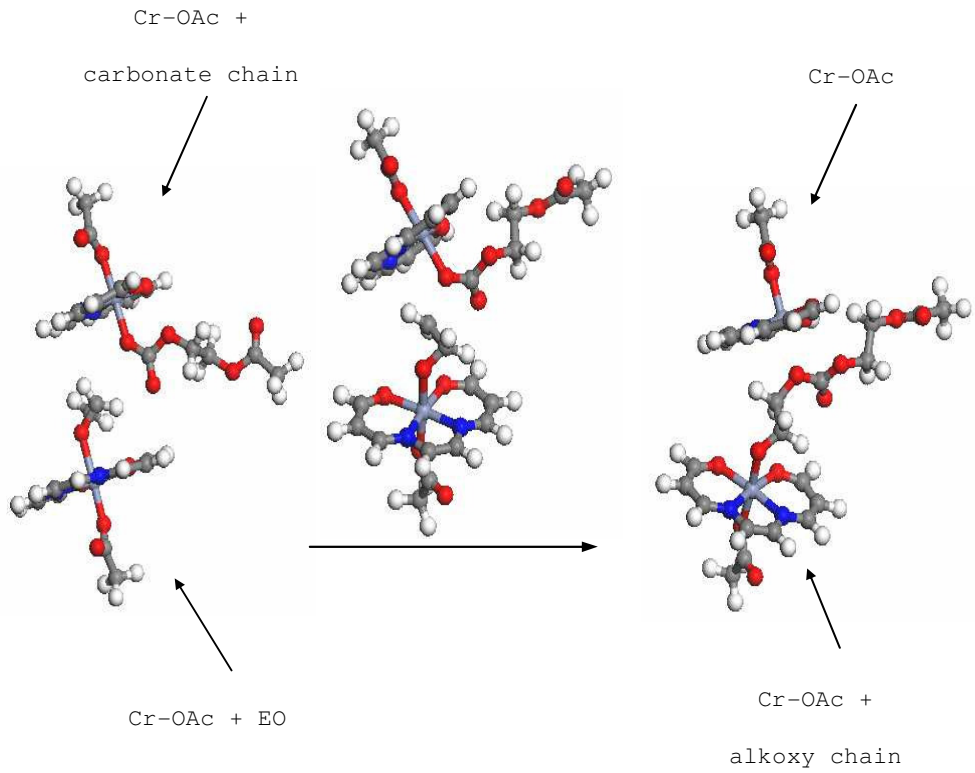


Figure 1 **Bimetallic mechanism of chain transfer and growth. A carbonate chain end group is transferred and ring-opens an activated epoxide.**

The insights obtained are in accordance with earlier investigations on the copolymerisation of PO and CO_2 with an essential role for more than one species. It can be concluded that functional copolymerisation systems must fulfil a few prerequisites: **A)** The presence of a species with an "adequately stable" carbonate group that does not undergo dissociation or induce backbiting. **B)** A Lewis acid that activates epoxides to such an extent that carbonate nucleophilic attack is feasible. **C)** A consecutive thermodynamically favourable carbonate transfer to the epoxide followed by CO_2 insertion. The system becomes simpler if one metal complex can serve all purposes.

A DFT study on chromium(III)-salophen complexes, performed by Dr. F. Molnar (BASF Aktiengesellschaft, Ludwigshafen), shows that low energy pathways for an alternating copolymerisation of ethylene oxide and carbon dioxide involve: **A)** Coordination of epoxide to a chromium(III)-metal centre. **B)** Attack of an external nucleophile or a metal-bound carbonate. **C)** Direct insertion of carbon dioxide in the metal-alkoxide bond. Copolymerisation is a smooth reaction if a metal

coordinated epoxide is attacked by a metal-bound carbonate. The *syn* opening of the epoxide ring was not found for any case with a low activation energy or negative reaction energy. Thermal decomposition of (metal-bound) polycarbonate proceeds more readily through a carbonate backbiting than through an alkoxide (leaving) group. Especially in the case of free carbonate chains decomposition is very efficient. Thus, the suppression of anion dissociation and formation of these species during catalysis are essential for the success. Anion dissociation is more facile in six-coordinate aluminium(III)-salophen complexes than in those of chromium(III)-salophen complexes.

Despite the recent breakthroughs, there are numerous challenges in the future. Currently, there are limited applications of epoxide-CO_2 copolymers due to their high cost and low thermal stability. Therefore, it will be necessary to develop systems that are capable to produce aliphatic polycarbonates economically. In addition, methods for producing these polymers with increased thermal stability are needed. So far, only chromium, aluminium, zinc and cobalt compounds have shown significant activity for the copolymerisation of epoxides and carbon dioxide. Alternative co-monomers, including lactones, aziridines, isocyanates, as well as new epoxides, such as styrene oxide, octane oxide and limonene oxide, will be promising reagents in the production of new block copolymers. Although the enantioselective copolymerisation of epoxides and carbon dioxide was accomplished, much higher levels of stereo-control as well as regio-control are required for improved physical properties of the materials. Homogeneous catalysts will lead to epoxide-CO_2 copolymers with unprecedented levels of architectural control, providing many new opportunities in polycarbonate science.

Further improvements in carbon dioxide utilisation reactions have to concern on the aspect to carry out reactions continuously rather than in a batch reaction. This will lead to a range of reactions which are not feasible in a conventional batch reactor. This system will be capable of producing large amounts of material in continuous mode and though, will be particularly relevant to fine chemical and pharmaceutical process chemistry. Typical examples include novel photochemical and microwave accelerated processes, including polymerisation reactions.

ZUSAMMENFASSUNG

Synthetische Polymere basieren größtenteils auf Erdöl. Da diese Werkstoffe nicht erneuerbar sind, besteht ein gesteigertes Interesse an der Entwicklung nachhaltiger Produkte. Die neuartigen Polymere sollten nicht nur aus erneuerbaren Quellen stammen, sondern möglichst auch biologisch abbaubar sein. Aliphatische Polycarbonate aus CO_2 und Propylenoxid besitzen das Potential, diese Anforderungen zu erfüllen (Abbildung 1).

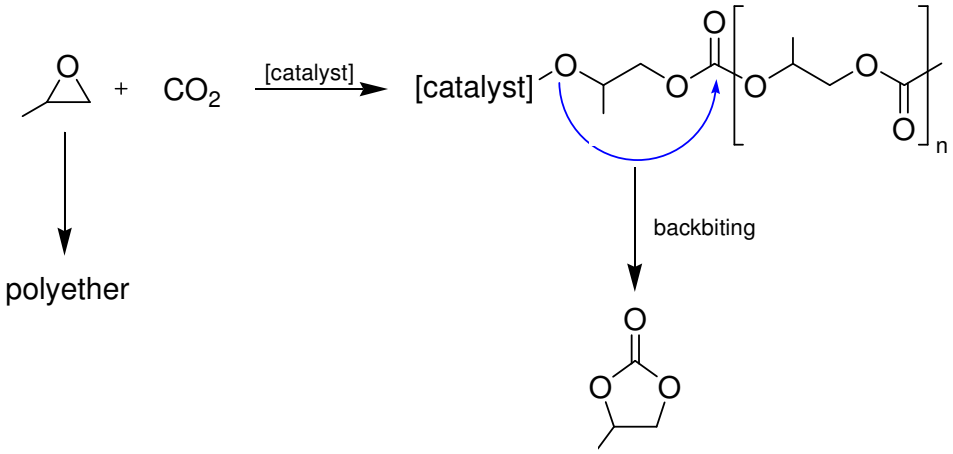


Abbildung 1 Copolymerisation von Propylenoxid und CO_2. Bildung zweier Nebenprodukte (Polyether und cyclisches Carbonat).

Im vergangenen Jahrzehnt wurden auf dem Gebiet der Epoxid-CO_2-Copolymerisation bedeutende Fortschritte erzielt. Im Vergleich zu ihren heterogenen Pendants ermöglichen homogene Katalysatoren schnellere und selektivere Epoxid-CO_2-Copolymerisationen. Maßgeschneiderte homogene Katalysatoren schaffen neue Perspektiven für die Verwendung von CO_2 und erlauben ein sehr viel tieferes mechanistisches Verständnis dieser Systeme. Ausgehend von preiswerten Epoxiden (z.B. Propylenoxid) ergeben sich mit den derzeitigen Katalysatoren geeignete Synthesewege zu einer Vielzahl von

Polycarbonaten wie Polypropylencarbonat, Polycyclohexencarbonat sowie zu Terpolymeren aus PO, CHO und CO_2. Es existieren Katalysatorsysteme, die es ermöglichen, Copolymere herzustellen, deren Molekulargewichte allein durch das Verhältnis von Monomer zu Initiator festgelegt sind. Mit geringfügigen Modifikationen im Katalysatordesign sind sowohl Polycarbonate als auch cyclische Carbonate mit hoher Geschwindigkeit und Selektivität synthetisierbar. Der Einsatz von homogenen Katalysatoren bietet zudem die Möglichkeit, durch Einstellung der Reaktionsbedingungen (Cokatalysator, Konzentration, Temperatur und Druck) die Bildung von Polycarbonaten und/oder cyclischen Carbonaten präzise zu steuern.

Die vorliegende Arbeit zeigt, dass das Katalysesystem aus einem homogenen Metall-Salophen-Katalysator und einem externen Nukleophil (Cokatalysator) die alternierende Copolymerisation von Propylenoxid und CO_2 ermöglicht. Diese Batch-Reaktion weist komplexe Abhängigkeiten von der Konzentration und dem Mischungsverhältnis aller Komponenten auf. Für das aliphatische Polypropylencarbonat (PPC) tritt die höchste Selektivität in einem bimetallischen System mit Chrom(III)-Salophen-Acetat und Aluminium(III)-Salophen-Chlorid als Katalysatoren bei 14 bar CO_2-Druck, 75°C, 3000 Äquivalenten Propylenoxid und 0,5 Äquivalenten Cokatalysator (NBu_4Cl) auf. Sowohl die Selektivität der Polycarbonatbildung als auch der Propylenoxidumsetzung zeigen einen parabolischen Verlauf der Abhängigkeit von der Cokatalysatormenge. Dies stützt die These eines bimetallischen Kettenwachstums, in welchem ein metallgebundenes Carbonat-Kettenende auf ein an einem anderen Metallzentrum koordiniertes (aktiviertes) Epoxid übertragen wird. Bemerkenswert ist, dass in Systemen, in denen ausschließlich Aluminium(III)-Salophen-Komplexe verwendet werden, keine Polycarbonatbildung auftritt, sondern ausschließlich cyclisches Propylencarbonat gebildet wird. Für das unterschiedliche katalytische Verhalten der Metallkomplexe wurden Modelle entwickelt, welche bei Einsatz von Chrom(III)-Salophen die Dissoziation eines Anions zeigen und bei Aluminium(III)-Salophen die CO_2-Insertion als geschwindigkeitsbestimmenden Schritt anführen.

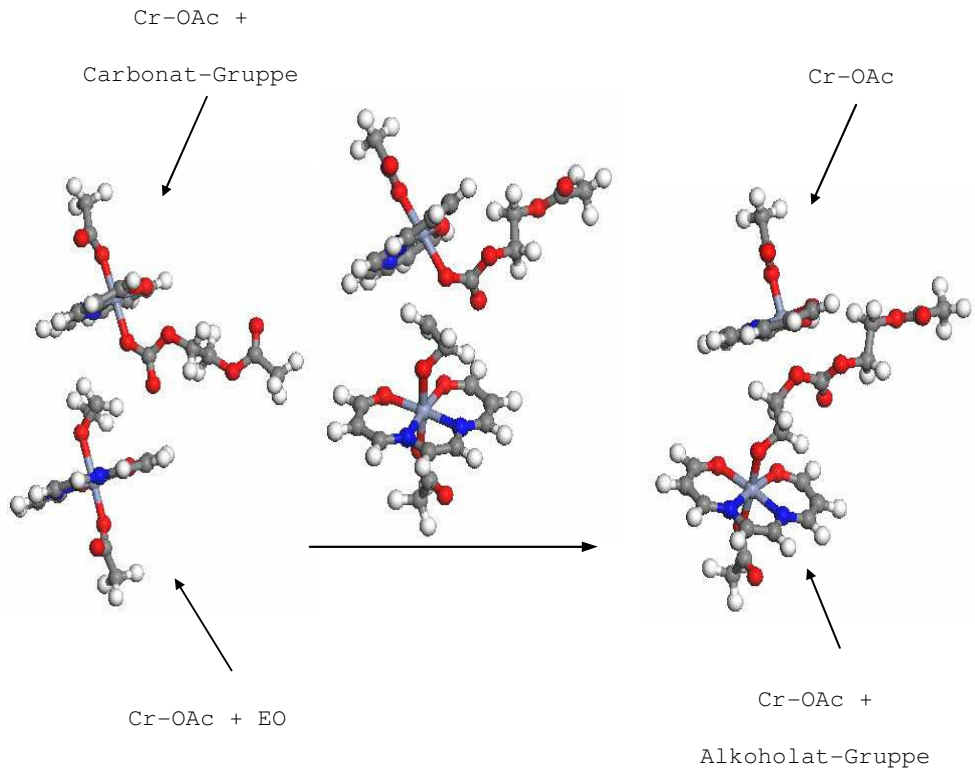


Abbildung 2 Bimetallischer Mechanismus des Kettenwachstums. Das Carbonatkettenende wird auf ein aktiviertes Epoxid übertragen.

Die Entwicklung eines bimetallischen Reaktionsmechanismus stimmt mit früheren Untersuchungen der Copolymerisation von Propylenoxid und CO_2 überein, welche die Existenz von mehr als einer Reaktionsspezies zu belegen versuchten. Daraus folgt, dass für eine funktionierende CO_2/PO-Copolymerisationsreaktion mehrere Grundvoraussetzungen erfüllt werden sollten: **A)** Eine ausreichende Bindung der Carbonatgruppe muss vorliegen, damit diese nicht dissoziieren und somit zu keinem internen Ringschluss führen kann. **B)** Ein nukleophiler Angriff der Carbonatgruppe muss aufgrund effektiver Aktivierung des Epoxids durch eine Lewis-Säure ermöglicht werden. **C)** Ein fortlaufender und thermodynamisch günstiger Transfer der Carbonatgruppe auf das Epoxid, gefolgt von einer CO_2-Insertion, muss stattfinden. Das System wird einfacher, sobald ein einzelner Metallkomplex alle Anforderungen erfüllen kann.

Dichtefunktionaltheorie (DFT) - Berechnungen von Chrom(III)-Salophen-Komplexen, durchgeführt von Dr. F. Molnar (BASF Aktiengesellschaft, Ludwigshafen), zeigen, dass für energiegünstige Reaktionswege bei der

alternierenden Copolymerisation von Ethylenoxid und CO_2 folgende Punkte berücksichtigt werden müssen: **A)** Koordination eines Epoxidmoleküls an ein Chrom(III)-Zentrum. **B)** Angriff eines externen Nukleophils oder einer metallgebundenen Carbonatgruppe. **C)** Insertion eines CO_2-Moleküls in die entstandene Metall-Alkoholat-Gruppe. Für die Ringöffnungsreaktion an einem einzelnen Metallzentrum konnte in diesen Berechnungen weder ein energiegünstiger Weg noch ein Weg mit einer negativen Reaktionsenergie gefunden werden. Der thermische Abbau einer metallgebundenen Polycarbonatkette verläuft schneller und einfacher via backbiting, wenn ein Carbonat und kein Alkoholat die Abgangsgruppe ist. Besonders bei einer freien Carbonatgruppe läuft der Kettenabbau sehr schnell ab. Deshalb ist die Unterdrückung der Dissoziation eines Anions und damit verbunden die Bildung eines freien Carbonatkettenendes für den Erfolg der Copolymerisation von entscheidender Wichtigkeit. Die Berechnungen konnten zeigen, dass eine Aniondissoziation in 6-fach koordinierten Aluminium(III)-Salophen-Komplexen leichter ist als in Chrom(III)-Salophen-Komplexen.

Trotz der jüngsten Fortschritte sind noch zahlreiche Aufgaben zu bewältigen. Wegen hoher Kosten und geringer thermischer Stabilität sind die Einsatzmöglichkeiten aliphatischer Polycarbonate derzeit eingeschränkt. Es müssen daher neue Katalysatorsysteme entwickelt werden, die in der Lage sind, Epoxid-CO_2-Copolymere kostengünstig zu erzeugen. Ein weiteres Ziel muss die Herstellung von Polycarbonaten mit erhöhter thermischer Stabilität sein. Bisher zeigten nur Chrom-, Aluminium-, Zink- und Kobaltverbindungen signifikante Aktivitäten in der Copolymerisation von Epoxiden und CO_2. Andere Comonomere wie Lactone, Aziridine, Isocyanate oder neue Epoxide wie Styroloxid, Oktenoxid und Limonenoxid bieten sich als vielversprechende Reagenzien für die Herstellung neuer Block-Copolymere an. Obwohl die enantioselektive Copolymerisation von Epoxiden und CO_2 bereits gelungen ist, sind zur Verbesserung der physikalischen Eigenschaften noch wesentlich höhere Grade an Stereo- und Regiokontrolle erforderlich. Homogene Katalysatoren werden die zielgerichtete Synthese von Epoxid-CO_2-Copolymeren mit festgelegten Materialeigenschaften ermöglichen und zahlreiche Perspektiven in der Polycarbonat-Forschung eröffnen.

Zukünftige Verbesserungen auf dem Gebiet der CO_2 -Nutzung für chemische Prozesse sollten auch darauf abzielen, Prozesse zu entwickeln, welche eine kontinuierliche Reaktionsführung erlauben und somit Batch-Reaktionen überflüssig machen. Dies würde Reaktionen ermöglichen, welche in gebräuchlichen Batch-Reaktoren nicht durchführbar sind. Eine kontinuierliche Prozessführung könnte dazu führen, dass Produkte in groß-industriellem Maßstab herstellbar wären, was insbesondere für die Produktion von Feinchemikalien und Pharmazeutika von großer Bedeutung ist. Neuartige photochemische und mikrowellenunterstützte Reaktionen sind Beispiele für solche Prozesse, u. a. auch bei Polymerisationsreaktionen.

DANKWORT

Ich möchte allen herzlich danken, die diese Arbeit ermöglicht und zu deren Erfolg beigetragen haben.

Mein Dank gilt Professor Dr. Dr. h.c. Bernhard Rieger für die Möglichkeit, dieses begeisternde Thema in seiner Arbeitsgruppe durchführen zu können. Danke für ideale Arbeitsbedingungen, den großen Freiraum, eigene Ideen verwirklichen zu können und die hilfreiche Unterstützung an geeigneter Stelle.

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Mein ganz besonderer Dank gilt meiner Familie für den Rückhalt, durch den sie mir diese Zeit hier in Ulm überhaupt erst ermöglicht hat. Besonders danken möchte ich meiner Frau Nadine, die während der gesamten Studien- und Promotionszeit voll hinter mir stand und mir dadurch viel Kraft und Ausdauer für meine Arbeiten gab.

EIDESSTATTLICHE ERKLÄRUNG

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbstständig und nur unter Verwendung der angeführten Quellen und Hilfsmittel angefertigt habe.

Ulm, 27. Oktober 2009 _____