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On the Formation of Aliphatic Polycarbonates from Epoxides with Chromium(III) and Aluminum(III) Metal–Salen Complexes

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Abstract: A DFT-based description is given of the CO_2/epoxide copolymerization with a catalyst system consisting of metal (chromium, iron, titanium, aluminum)–salen complexes (salen = *N,N'*-bis(3,5-di-*tert*-butylsalicyliden-1,6-diaminophenyl) in combination with either chloride, acetate, or dimethylamino pyridine (DMAP) as external nucleophile. Calculations indicate that initiation proceeds through nucleophilic attack at a metal-coordinated epoxide, and the most likely propagation reaction is a bimolecular process in which a metal-bound nucleophile attacks a metal-bound epoxide. Carbon dioxide insertion occurs at a single metal center and is most likely the rate-determining step at low pressure. The prevalent chain terminating/degradation—the so-called backbiting, a reaction leading to formation of cyclic carbonate from the polymer chain—would involve attack of a carbonate nucleophile rather than an alkoxide at the last unit of the growing chain. The backbiting of a free carbonato chain end is particularly efficient. Anion dissociation from six-coordinate aluminum is appreciably easier than from chromium–salen complexes, indicating the reason why in the former case cyclic carbonate is the sole product. Experimental data were gathered for a series of chromium–, aluminum–, iron–, and zinc–salen complexes, which were used in combination with external nucleophiles like DMAP and mainly (tetraalkyl ammonium) chloride/acetate. Aluminum complexes transform PO (propylene oxide) and CO_2 to give exclusively propylene carbonate. This is explained by rapid carbonate anion dissociation from a six-coordinate complex and cyclic formation. CO_2 insertion or nucleophilic attack of an external nucleophile at a coordinated epoxide (at higher CO_2 pressure) are the rate-determining steps. Catalysis with [Cr(salen)(acetate/chloride)] complexes leads to the formation of both cyclic carbonate and polypropylene carbonate with various quantities of ether linkages. The dependence of the activity and selectivity on the CO_2 pressure, added nucleophile, reaction temperature, and catalyst concentration is complex. A mechanistic description for the chromium–salen catalysis is proposed comprising a multistep and multicenter reaction cycle. PO and CO_2 were also treated with mixtures of aluminum– and chromium–salen complexes to yield unexpected ratios of polypropylene carbonate and cyclic propylene carbonate.

Keywords: carbon dioxide fixation · copolymerization · epoxides · homogeneous catalysis · polycarbonates

Introduction

The formation of aliphatic polycarbonates from epoxides and carbon dioxide, as shown in Scheme 1, can be achieved if an appropriate catalyst system is present.[1–7] The nature of the catalyst is key to the copolymerization reaction. Several side reactions may occur, which involve polyether or cyclic carbonate formation (Scheme 1). Ethylene oxide (EO) and 1-alkyl-substituted oxiranes are especially difficult to copolymerize, because of the facile formation of cyclic products through a so-called backbiting reaction, a putative intramolecular reaction in which a metal-bound alkoxy chain end is presumed to attack the nearest carbonyl carbon atom in the chain. This behavior has been explained by the high configu-

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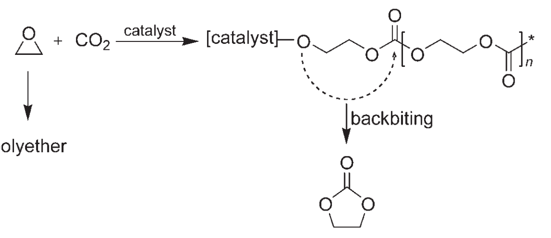


Scheme 1. Copolymerization scheme of EO and CO_2. Formation of cyclic carbonate occurs as a side reaction. Mechanism of cyclic carbonate formation is depicted as it is discussed in the literature.

rational mobility of the carbonate chain derived from such 1-alkyl-epoxides that would facilitate the formation of cyclic byproducts. It is in marked contrast to, for example, the copolymerization of cyclohexene oxide (CHO) and CO_2, which are much more easily transformed into the corresponding polycarbonate (PCHC: polycyclohexylcarbonate).

The copolymerization of epoxides and carbon dioxide was first reported by Inoue in the 1960s, using the heterogeneous catalyst prepared by reaction of diethyl zinc and one equivalent of water.[8,9] Today, zinc dialkyls remain important starting materials for the synthesis of active epoxide/carbon dioxide copolymerization catalysts. Through reaction with active proton-containing compounds more or less effective catalytic systems are obtained.[10] These protonation reagents include alcohols,[11–15] (polyhydridic) phenols,[16,17] carboxylic acids,[18] enols,[19] primary amines,[20,21] and macrocycles.[2] More recently this list was extended by diketiminates.[22–30] An effective modern catalyst system is, for example, also created from a mixture of $ZnEt_2$, glycerine and 0.05 equivalents of a rare earth metal salt.[14,31–34] Catalyst formation usually proceeds through the fast protonolysis of one of the zinc–alkyl bonds and ultimately to compounds that not necessarily contain zinc–alkyl entities. In general, agglomerates with several (different) zinc centers are formed (vide infra). There is no essential role for the zinc–ethyl entity as chain starter. Insertion of either CO_2 or epoxide into the zinc–alkyl bond is sluggish.[7,35] Therefore zinc–diamides can also be effectively be used as starting materials.[36,37] The more ionic zinc–amide bonds are readily doubly substituted through reaction with the protonating agents, for example, to yield active catalysts such as $Zn(OR)_2$ (R = aracyl, aryl).[38]

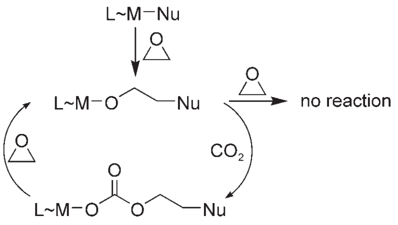
Zinc carboxylate copolymerization catalysts prepared from salts like zinc oxide, zinc carbonates and/or hydroxides and carboxylic acids are more convenient to handle and utilize cheaper starting materials. A preferred catalyst is prepared from glutaric acid,[5,39,40] but also zinc compounds prepared from adipinic,[41] pimelic,[42] phthalic,[43] or mixtures of carboxylic acids[44] show activity.[45] This type of catalyst is preferentially used for the commercial preparation of aliphatic polycarbonates starting from EO or mono-substituted oxiranes, as they give high-molecular-weight polycarbonates with a high carbonate content and little formation of cyclic byproducts.[41,46] Recently, a substantial body of reports appeared dealing with the heterogeneous zinc dicarboxylate systems. For example, Kim et al. performed an extensive study on the structure of the catalyst and the interactions of the solid with both monomers.[47–49]

Some mechanistic insights into the copolymerization with the various (heterogeneous) zinc catalysts have been reported. An early study by Inoue on the copolymerization of cyclohexene oxide and carbon dioxide shows the coordinated epoxide to be nucleophilically attacked from the backside, unusual and unexpected for a single-site catalysis, with *syn* insertion at the metal center as it is operative in olefin chemistry.[50] 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).[18,51] Kuran et al. confirmed Inoue's experiments and in addition found substituent effects when applying functionalized phenols.[52,53] Related results were reported for example by Rätsch and Haubold for the $ZnEt_2/H_2O$ system.[54] They found that the most active system contains a zinc–ethyl entity next to zinc–oxyhydroxy 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, in contrast to single-site catalysis, has definitely been present in the early copolymerization catalysis research.

In a more straightforward study on the copolymerization of PO (propylene oxide) and CO_2 with aluminum porphyrins a direct bimolecular reaction mode of the epoxide opening was proposed.[55,56] Also, Jacobson reports several studies in which the derivatization of epoxides is described with macrocyclic metallo compounds, in which several centers work in concert.[57] Recently also Coates interprets his results with zinc–diketiminates as catalysts for the CHO/CO_2 and limonene oxide/CO_2 reaction in terms of a multisite catalysis mechanism.[25,30] This is in contrast, for example, to work by the group of Darensbourg on a catalyst system composed of chromium–salen (salen = *N*,*N'*-bis(3,5-di-*tert*-butylsalicyliden-1,6-diaminophenyl) and an axial ligating compound, or to work by Chisholm on tetraphenylporphyrin aluminum complexes, and a quantum chemical study by Morokuma on the copolymerization of cyclohexene oxide and CO_2.[58–60] Also discrete manganese and cobalt macrocyclic systems have recently been reported that catalyze the copolymerization.[61–63] Here another type of bimolecular reaction is proposed.

Evidently, the copolymerization of epoxides and carbon dioxide is not a simple process. A formal general scheme for a copolymerization system based on metal compounds can be formulated with the following elementary steps: 1) formation of a chain starting group through epoxide ring-opening, 2) preferred CO_2 insertion, and 3) epoxide ring-opening with concomitant carbonate nucleophile addition (Scheme 2).

In this scheme, the alkoxide group should have a relatively limited reactivity—in best case no nucleophilicity—



Scheme 2. Copolymerization reaction scheme (Nu = nucleophile; L = ligand system or crystal surface).

toward epoxides, avoiding the thermodynamically favorable polyether formation, and, on the other hand, insertion of CO_2 into the alkoxide–metal bond and/or the consecutive reaction with an epoxide entity should at least be competitive. In addition the intramolecular backbiting reaction should be suppressed; no nucleophilic attack on the growing chain should occur. Such a rudimentary scheme should be further specified with respect to the prerequisites of the metal center of the mediator. So far zinc seems the metal of choice; however, in several ligations, active catalysts are formed (vide supra) with Cr^{III} (and other transition metals) in macrocyclic ligand environments. These last complexes are more readily investigated, since many zinc catalysts are solids or complex aggregates.

We wish here to report on a quantum chemical and experimental study of the copolymerization of epoxides and CO_2 with such complexes. The Cr^{III}–salen entity and related aluminum–salen complexes are considered in detail. Combined theoretical and experimental studies on the mechanism of the reaction are rarely reported, in fact theoretical descriptions of epoxide polymerization reactions are only emerging (vide supra). The chromium catalysts with macrocyclic ligands in form of a salen or porphyrin work as discrete homogenous catalysts in solution.[64] They seem to form good model systems for the copolymerization reaction of EO or PO and CO_2. The compounds may be used to convert PO to either polypropylene carbonate (PPC), cyclic propylene carbonate (cPC), or polypropylene oxide (PPO), depending on the addition of a co-reagent. Nguyen reported that in the Cr^{III}–salen/DMAP (dimethylamino pyridine) system with a 1:1 ratio of catalyst/activator a very efficient formation of cPC from PO and CO_2 occurs.[65] We showed that the Cr^{III}–salen/DMAP system can be turned into a PPC producing catalyst system provided that the ratio of Cr/DMAP is larger than 1, with an optimum polymer yield at a ratio of approximately 4.[35] If DMAP is omitted no PO conversion is found. This parallels the observations by Darensbourg on the Cr^{III}–salen/imidazole system.[58] Several (putative multicentered) reactions, including initiation, propagation, chain transfers, termination, chain decomposition in combination with metal coordination/decoordination, may take place. These reactions will be considered in detail.

Results and Discussion

Theoretical study

Catalytic cycle leading to the formation of polycarbonates: The most challenging reaction in the system of epoxides and CO_2 is the formation of aliphatic polycarbonates: they are the thermodynamically unfavorable products relative to polyether and cyclic carbonate.[66] The chromium–salen catalyst **1a**-Cl along with the reduced model **1b**-Cl used in many of the calculations is depicted in Figure 1. Calculations were carried out with **1b** if not stated otherwise.

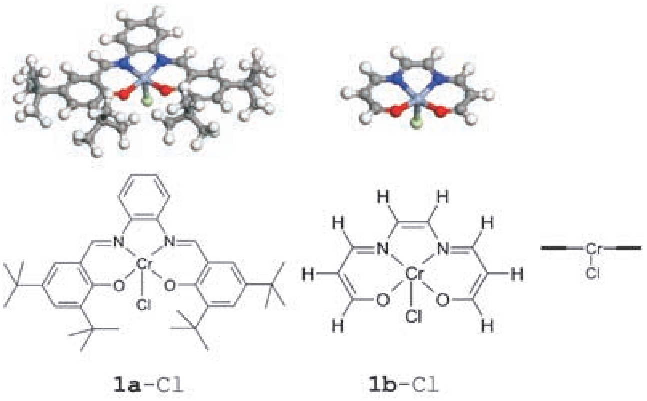


Figure 1. Salen catalyst (**1a**-Cl) and the reduced model compound (**1b**-Cl) used in the calculations.

We started our theoretical investigation considering the alternating insertion of ethylene oxide and CO_2 at the chromium center of the model compound **1b**-Cl. However, in spite of numerous attempts, calculations did not reveal a chemically attractive, low-energy pathway for EO ring-opening and insertion into the chromium–chloride bond at the metal center. Attention was subsequently directed to the EO coordination reaction of **1b**-Cl or **1b**-OAc leading to an activated monomer. Coordination is found to be an exothermic reaction with factually no activation energy as shown in Figure 2. It may thus be assumed, that any free coordination

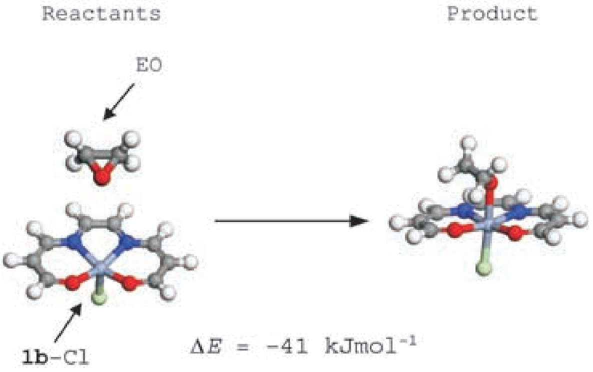


Figure 2. Initial coordination of ethylene oxide to the chromium–salen model complex **1b**-Cl.

site on a five-coordinate chromium–salen complex is rapidly occupied by an epoxide, certainly in neat epoxide.

The next step considered, leading to the formation of an alkoxy chain end, is the attack of an external nucleophile, for example, acetate, on the epoxide carbon atoms. The attack was found to proceed smoothly in an Sn2 like fashion leading to a coordinated alkoxide (Figure 3) and a six-coordinate (negatively charged) chromium complex. The function of the chromium complex is of a dedicated Lewis acid that polarizes and activates the epoxide, and is capable of forming a stable metalate complex. The reaction has major similarities to what has been described for the formation of lactones from epoxides and CO.[67] The activation barrier for the nucleophilic attack is negligible (2 kJ mol^{-1}) and the reaction energy amounts to -123 kJ mol^{-1}.

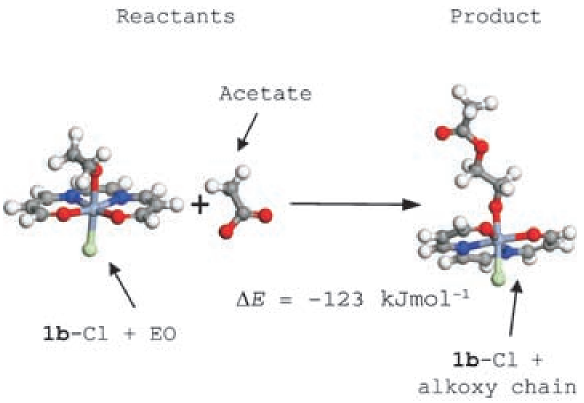


Figure 3. Initial ring-opening event of ethylene oxide by an acetate anion at complex **1b**-Cl.

The identical reaction with chloride (ΔE of -95 kJ mol^{-1}) or DMAP (ΔE of -85 kJ mol^{-1}) as external nucleophile also proceeds exothermally. In case of the neutral DMAP nucleophile an appreciable activation barrier is found of $\Delta E^{\neq} = 42$ kJ mol^{-1}. The analogous salen complexes containing Ti^{III}, Fe^{III}, and Co^{III} as central metal ion were also considered in this type of reaction (Table 1). Likewise, it was found that the ring-opening event occurred easily. The activation energies increase from Ti^{III} to Co^{III}, possibly reflecting the decreasing Lewis acidity of the central metal ion. The reaction energies were large and negative in all cases. Thus an anionic six-coordinate complex is formed, the initial step into a catalytic cycle as depicted in Scheme 2.

Table 1. Ring-opening of EO at various [metal(salen)Cl] complexes with acetate ($^{-}$OAc).

	Cr^{III}	Ti^{III}	Al^{III}	Fe^{III}	Co^{III}
$\Delta E^{\neq}$ [kJ mol^{-1}]	2	5	5	12	29
ΔE [kJ mol^{-1}]	-123	-129	-119	-115	-83

To assess the impact of the use of the reduced ligand system, calculations were also performed for the experimentally relevant chromium(III)–salen complex with structure **1a**-Cl (Figure 1) and also on the analogues with unsubstituted salen rings, with chloride coordinating in the axial position and chloride as external nucleophile (on EO and PO). A consistently negligible activation energy and a strong negative reaction energy of approximately -95 kJ mol^{-1} results for the ring-opening event in all cases. It shows that the main factors are electronic in origin and that the use of the reduced model **1b** should give relevant results.

For a cationic four-coordinate Cr^{III}–salen complex (without a *trans* anion), the ring-opening reaction proceeds even without a barrier both for acetate ($\Delta E = -210$ kJ mol^{-1}) and DMAP ($\Delta E = -170$ kJ mol^{-1}) as nucleophiles. A comparable cationic Al^{III} complex shows a (small) barrier and is less exothermic in the reaction with an acetate nucleophile ($\Delta E^{\neq} = 33$ kJ mol^{-1}, $\Delta E = -67$ kJ mol^{-1}). Generally, the effective Lewis acidity of aluminum–salen complexes is expected to be smaller than that of chromium complexes.

It is concluded that ring-opening of a (1-alkyl)epoxide coordinated to a metal–salen complex proceeds smoothly through a backside attack of an external nucleophile, whereas a background reaction of these nucleophiles and epoxide is much slower. This was only to be expected. Insertion into a metal–nucleophile bond in one step, however, was not found to be energetically feasible.

The consecutive insertion of carbon dioxide into the formed metal alkoxide was presumed to be a simple intramolecular process. Indeed, a low-energy pathway for the insertion of CO$_2$ occurring in a *syn* fashion at the metal center could be located for the negatively charged [Cr(salen)(alkoxide)] and [Fe(salen)(alkoxide)] (six-coordinate) complexes. No such pathway is available for the titanium derivative. The [Fe^{III}(salen)(alkoxy acetate)] complex reacts through a transition state that involves symmetric distortion of the salen ring system (Figure 4). The activation energy for CO$_2$ insertion was found to proceed through a barrier $\Delta E^{\neq} = 43$ kJ mol^{-1} and a reaction energy $\Delta E = -10$ kJ mol^{-1}. For aluminum an activation barrier $\Delta E^{\neq} = 99$ kJ mol^{-1} with an energy $\Delta E = +70$ kJ mol^{-1} is found. A comparable path-

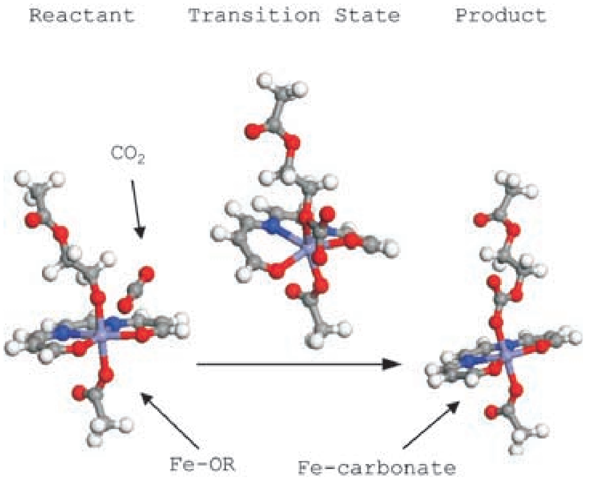


Figure 4. Insertion of CO$_2$ in the salen Fe–OR bond.

way for CO_2 insertion into an analogous six-coordinate chromium(III)–alkoxide bond was not found; here an open coordination site needs to be created through de-coordinative rotation of one of the phenoxy oxygen atoms of the salen ligand. The creation of this empty coordination site requires approximately $\Delta E = +80\,kJ\,mol^{-1}$ with a barrier $\Delta E^{+} = +100\,kJ\,mol^{-1}$. The CO_2 insertion reaction in this activated complex then only has a very small barrier ($5\,kJ\,mol^{-1}$) with a reaction energy of $-12\,kJ\,mol^{-1}$. Re-coordination of the salen phenoxide results in a gain in $\Delta E = -80\,kJ\,mol^{-1}$ and the overall insertion becomes slightly exothermic. For aluminum, the activation barrier for CO_2 insertion in the open conformation—which lies approximately $40\,kJ\,mol^{-1}$ higher in energy—is $\Delta E^{+} = +49\,kJ\,mol^{-1}$ and is basically thermoneutral ($\Delta E = 2\,kJ\,mol^{-1}$).

The insertion of CO_2 in the five-coordinate complexes of Cr^{III}– and Al^{III}–salen was found to proceed through the same symmetrical *syn* transition state as the anionic Fe^{III} complex. The barrier and reaction energies are 45 and $24\,kJ\,mol^{-1}$, respectively, for Cr^{III}, and 38 and $-24\,kJ\,mol^{-1}$, respectively, for Al^{III}. Thus anion de-coordination or intermolecular anion exchange with putatively present five-coordinate complexes may open an alternative low-energy CO_2 insertion reaction channel. Such a sequence would probably be a preferred mode.

After the formation of the carbonate chain end, the next step of a functional alternating copolymerization requires addition of a further epoxide. As already found for the initiation reaction in the **1b**-OAc species, an attractive route could not be detected for a *syn* insertion at a single metal center, which does not have a five-coordinate geometry. However, a comparable alternative low-energy pathway was detected as soon as reactions between a [Cr(salen)(carbonate)] complex and a second metal center carrying an activated epoxide were allowed. In the productive step, the carbonate group was transferred from one metal center 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 center. The process is depicted in Figure 5. The attack may proceed either with the C=O moiety or with the carbonato metal oxygen atom. They show somewhat different activation energies, but all within a plausible range for reaction to occur at ambient temperature. Details of the transfer mechanisms are given in Table 2. The activation barrier was also determined for the formation of a polyether, that is, the analogous attack of a chromium-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 catalysis may thus be expected to competitive at low carbon dioxide concentration. Moreover, the effect of high- and low-spin states of the two-center chromium complex on the reactivity was studied. From the data collected in Table 2 it becomes clear that there is no strong dependence on spin state.

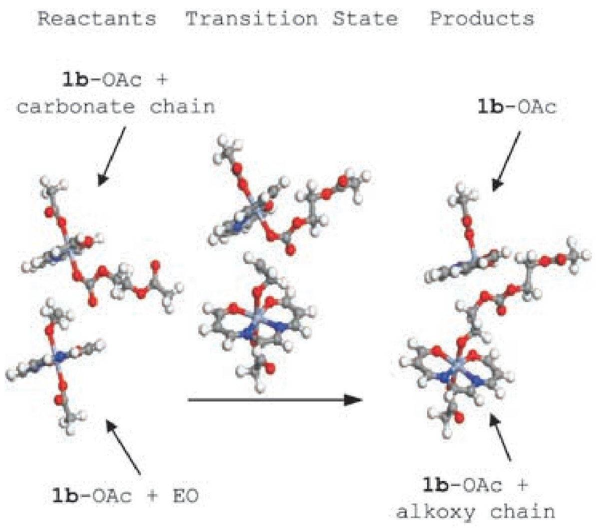


Figure 5. Chain transfer and growth, a carbonate chain end group is transferred and ring-opens an activated epoxide. Acetate ligands in the *trans* position.

For the alkoxide transfer no transition state could be located on the triplet surface.

The influence of the *trans* ligand on the activation of the epoxide was also addressed in the transition state of the chain-growing transfer reaction.[59] The activation barrier and reaction energy is lower for a process in which the epoxide is coordinated to a chromium metal center with DMAP in the *trans* position (septet transition state, no major influence of the spin states found) with $\Delta E^{+} = 27\,kJ\,mol^{-1}$ and $\Delta E = -70\,kJ\,mol^{-1}$ for a carbonate (M−O) attack. This is due to the enhanced polarization of the epoxide. In the case of Al^{III}–salen with a *trans* bound acetate moiety an activation energy $\Delta E^{+} = 30\,kJ\,mol^{-1}$ and an enthalpy $\Delta E = -22\,kJ\,mol^{-1}$ was found. The activation barriers for bimolecular ring-opening at chromium and aluminum salen complexes are thus very much in the same range.

Cyclic carbonate formation: Chain growth through alternating repetition of the above reaction will only occur if two complexes meet in an appropriate orientation. Therefore, the metal–carbonato and –alkoxy species must be stable enough to prevent side reactions, such as formation of cyclic carbonates (vide infra). Evidently, understanding the factors controlling the backbiting process is of eminent impor-

Table 2. Chain transfer (epoxide opening) with complex **1b**-OAc.

	Septet		Quintet		Triplet	
	ΔE^{+} [$kJ\,mol^{-1}$]	ΔE [$kJ\,mol^{-1}$]	ΔE^{+} [$kJ\,mol^{-1}$]	ΔE [$kJ\,mol^{-1}$]	ΔE^{+} [$kJ\,mol^{-1}$]	ΔE [$kJ\,mol^{-1}$]
carbonato (−O)	51	8	39	−13	41	−12
carbonate (=O)	28	−23	32	−22	29	−30
alkoxide (−O)	16	−72	22	−72	–	–

tance for the design of a copolymerization system. We investigated several routes leading to cyclic carbonates (Scheme 3). These are backbiting of an alkoxy end group—the process usually discussed—and backbiting of a carbonate group.[85] Additionally, during the process of cyclic carbonate formation, the chain may be either free or bound to the metal center.

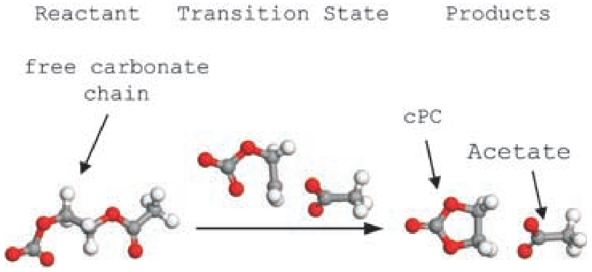
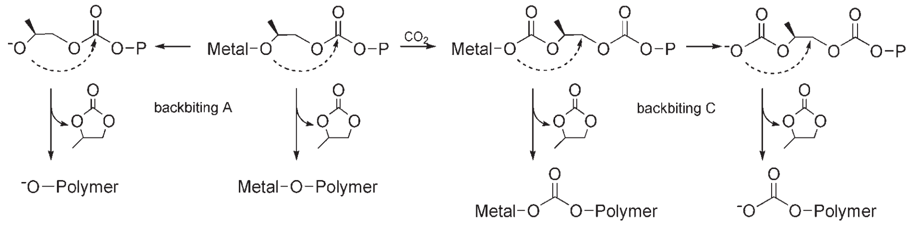


Figure 7. Carbonate formation through free carbonate chain end. Acetate ion (initiator) is shown as leaving group. Same mechanism for carbonate as leaving group.

Calculations indicate that backbiting of the carbonate end group has appreciably lower activation energies than of the alkoxy moiety, either in the metal-bound or "free" anionic form. In addition, free carboxylato chains decompose to cyclic structures with the smallest activation energies. In detail, formation of a cyclic carbonate starting from a carbonate group attached to **1b**-OAc (Figure 6) has an activation energy $\Delta E^{\neq} = 95\,\text{kJ}\,\text{mol}^{-1}$ ($\Delta E = +68\,\text{kJ}\,\text{mol}^{-1}$). These numbers are 90 and $60\,\text{kJ}\,\text{mol}^{-1}$, respectively, for **1b**-Cl and 132 and $123\,\text{kJ}\,\text{mol}^{-1}$, respectively, for **1b**-DMAP. Thus, the more acidic the metal center, the higher the activation barriers appear. For a free carbonate chain end on the other hand, formation of cyclic carbonate is a very simple reaction with an activation barrier and a reaction energy of 35 and of $-45\,\text{kJ}\,\text{mol}^{-1}$, respectively, for ethylene carbonate, and 45 and $-55\,\text{kJ}\,\text{mol}^{-1}$, respectively, for propylene carbonate formation (Figure 7). For the Al^{III}–salen/chloride system, the energetics of cyclic carbonate formation at the metal center are very similar to the corresponding Cr^{III} system ($\Delta E^{\neq} = 93\,\text{kJ}\,\text{mol}^{-1}$, $\Delta E = +65\,\text{kJ}\,\text{mol}^{-1}$, six-coordinate complex).



Scheme 3. Formation of cyclic carbonate. Possible routes for the formation are through an alkoxy or carbonate chain end.

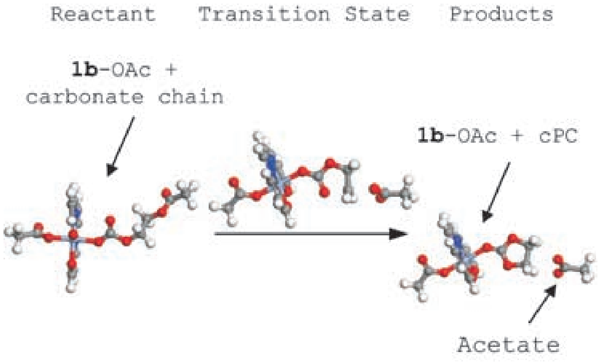


Figure 6. Metal-centered cyclic carbonate formation. Acetate ion (initiator) is shown as leaving group. Same mechanism for carbonate as leaving group.

For alkoxy chain ends on the other hand—both for the metal-bound and the free species—no low-energy pathway for cyclic carbonate formation was detected in the model calculations. These findings can be rationalized by considering the character of the leaving group during formation of the cyclic carbonate. In the case of an alkoxy nucleophile, the strongly nucleophilic aliphatic alcoholate is also the leaving group: a very weak leaving group compared to the much more stable carbonato group of the alternative pathway. An uncatalyzed "intrachain" mechanism for cyclic carbonate formation as depicted in Figure 8 is very unlikely due to the considerably higher energy barrier for this process.[70]

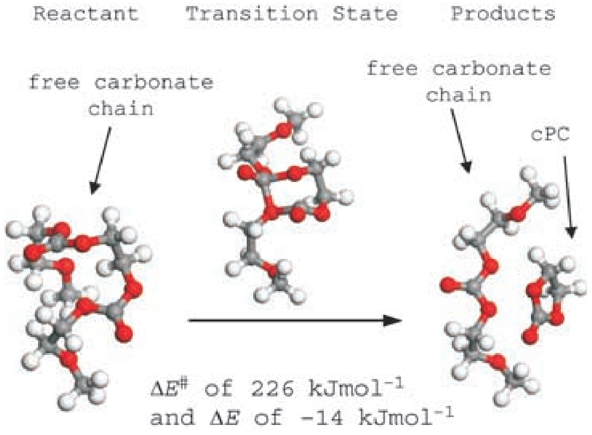
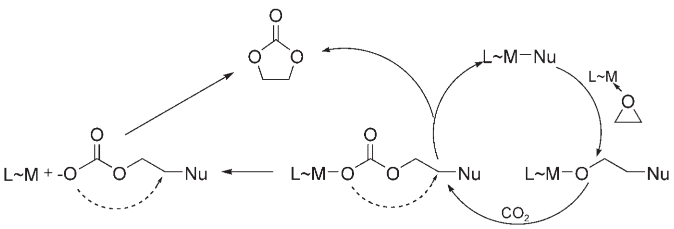


Figure 8. Intrachain formation of cyclic carbonate.

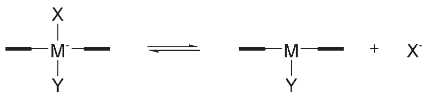
Note that a similar pathway is available to account for the efficient formation of cyclic carbonate reported by Nguyen[65] and Kim in case of the $ZnBr_2$/pyridine system[71] (Scheme 4). Nguyen recently proposed a related mechanism for the ring expansion of aziridines with CO_2.[72]



Scheme 4. Formal pathways for the formation of cyclic carbonate from epoxides and CO_2.

Hence, it is of importance to have knowledge about the binding energies of anions in various six-coordinate metal–salen complexes. Anion dissociation from six-coordinate complexes is expected to be of most relevance, spontaneous dissociation from five-coordinate neutral species is very much more unlikely. Results are in Table 3 for selected chromium, iron, and aluminum complexes, in part for the reduced salen system, and the unsubstituted chromium complex **1a**-*t*Bu. Again, binding energies appear to be largely determined by the electronics of the system. It is also easily recognized that alkoxide ligands form stronger bonds than carbonate groups. Of interest is also the dependence of the dissociation energy on the *trans* ligand Y. The higher the nucleophilicity of Y, the more facile dissociation of X may occur; for example, the carbonate group in chromium– or iron(III)–salen complexes would dissociate more readily in an alkoxy–carbonate than in a carbonate–carbonate configuration. For aluminum–salen complexes it is found that anion dissociation is energetically more favorable than in comparable chromium complexes. This is also of importance for the CO_2 insertion pathway: five-coordinate species are easily generated here that open a low-energy pathway for carbonate formation (Figure 9).

Table 3. Carbonate, acetate, and alkoxide chains on both “sides” of a [M(salen)(X)(Y)] complex with X as leaving anion.



$$X{-}M^{-}(Y) \rightleftharpoons M(Y) + X^{-}$$

M	X	Y	**1b**-Y $\Delta E_{M\text{-}X}$ [kJmol^{-1}]	**1a**-*t*Bu-Y $\Delta E_{M\text{-}X}$ [kJmol^{-1}]	**1b**-Y ΔG [kJmol^{-1}]
Cr	OR	OC(O)OR	258	268	
	OR	OR	223	232	
	OC(O)OR	OR	120	126	
	OC(O)OR	OC(O)OR	144	146	
Fe	OR	OC(O)OR	268		
	OR	OR	180		
	OC(O)OR	OR	119		
	OC(O)OR	OC(O)OR	127		
Cr	OAc	OC(O)OR	188		142
	OC(O)OR	OAc	127		80
Al	OAc	OC(O)OR	158		99
	OC(O)OR	OAc	95		45

Free carbonato groups next to metal-based ones can also act as nucleophiles in a bimolecular reaction for the ring-opening of coordinated epoxides with $\Delta E^{\neq} = 8\,\mathrm{kJ\,mol^{-1}}$ and $\Delta E = -82\,\mathrm{kJ\,mol^{-1}}$. Hence, this bimolecular recombination may stabilize a PO/CO_2 copolymerization catalysis system.

It may thus be anticipated that during and after a polymerization reaction, polymer degradation may start via the formation of free carbonate chains. Quenching the polymerization reaction by transformation of the carbonate chain end is thus essential for the final polymer stability. Thus, effectively quenching the polymerization reaction mixture and end capping the polymer helps to obtain a thermally more robust polycarbonate. From thermolysis studies it is accordingly known that the low-temperature polymer-decomposition route involves unzipping of chains, rather than chain scission.[73]

We can now summarize the data for coreacting epoxides and carbon dioxide in the presence of chromium– and aluminum–salen complexes in form of an energy profile. The energy (ΔE) is depicted in Figure 9 for the copolymerization, including initiation with a nucleophile and termination along two pathways—cyclic carbonate formation at the metal to give carbonate-coordinated salen complexes or dissociation of the growing chain followed by the formation of cyclic carbonate. In case of aluminum, the not observed polymerization reaction through nucleophilic attack of a metal carbonate species onto a coordinated ethylene oxide is also depicted. The activation energy lies substantially under that of termination in form of a cyclic carbonate formation. It should be noted that only the energy of reaction is depicted and thus important entropy contributions to ΔG are not considered. It may, for example, be anticipated that CO_2 insertion and bimolecular epoxide opening have an appreciable negative entropy, leading to a substantially higher Gibbs energy, and that, in contrast, anion dissociation and, to a lesser extent, decomposition of carbonate species at the metal have smaller Gibbs barriers than expected on the basis of their energies. Gibbs activation energies for anion dissociation may be even lower than those of decomposition to cyclic carbonate. Gibbs energies are given for anion dissociation of chromium and aluminum acetate–carbonate complexes in Table 3 to illustrate this point. Nevertheless, Figure 9 gives an impression of the reaction pathways of PO and CO_2 transformations mediated by the two complexes. In addition, CO_2 insertion for five-coordinate species is depicted as the major reaction channel without taking de- and recoordination of the *trans* anion into consideration in the energy plot. The energy differences between five- and six-coordinate species are not considered essential, as intermolecular exchange of anions through innersphere exchange reactions will have low barriers and energies.

The insertion of carbon dioxide into the metal alkoxide has the highest activation energy in the scheme for Al. Since it is a bimolecular reaction, Gibbs energies will be even higher. Carbon dioxide insertion may well be the rate-determining process, certainly at lower CO_2 pressure. The main difference between aluminum and chromium catalysis is the ease of anion dissociation; these should be very decisive for their catalytic action because of the fast decomposition of

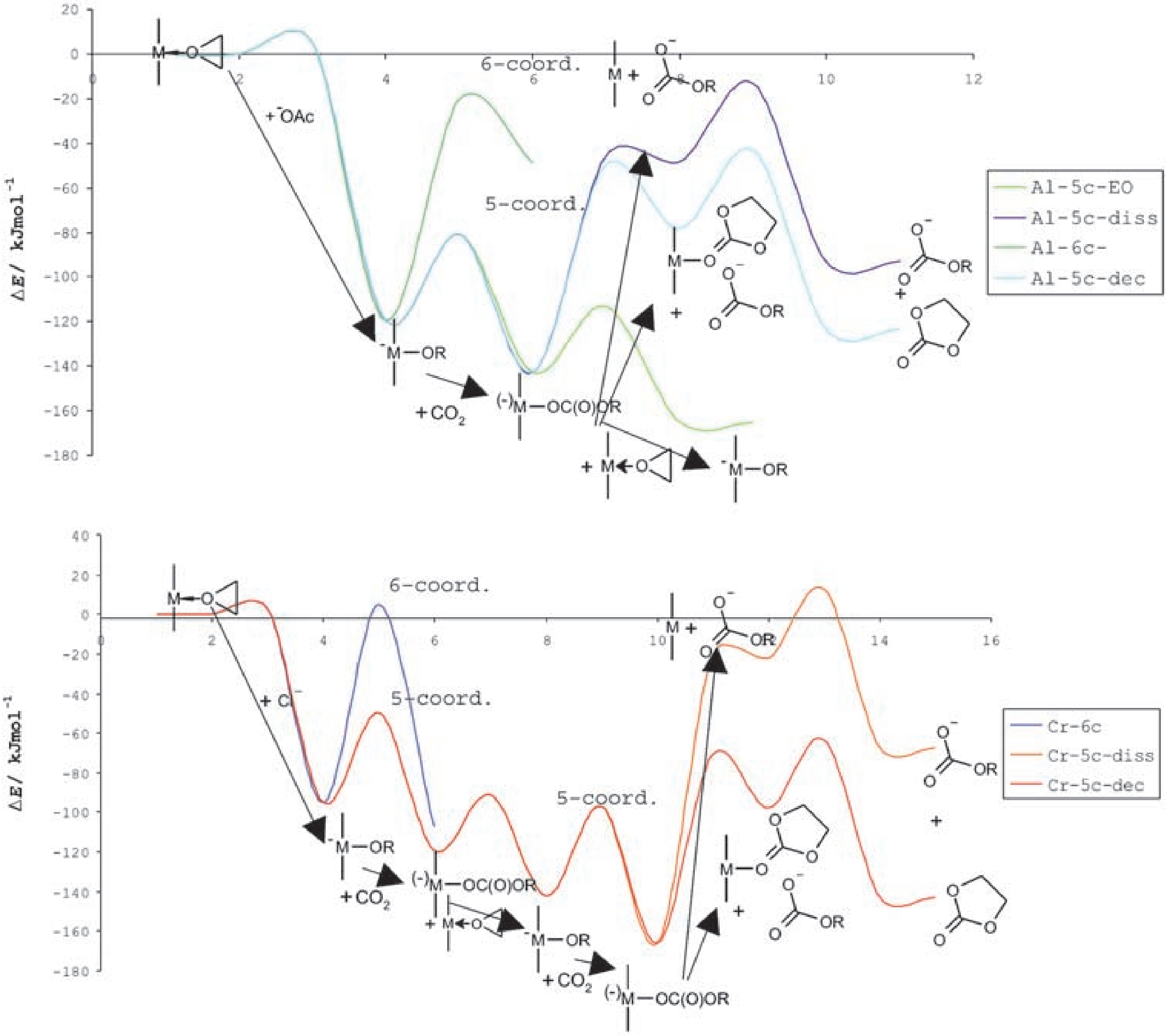


Figure 9. Reaction enthalpies for the epoxide/carbon dioxide PO/CO_2 coreacting system in the presence of aluminum– (top) and chromium–salen (bottom) complexes.

carbonato chain ends (vide supra). The formation of polyether in case of chromium–salen complexes through bimolecular reaction of metal alkoxide and coordinated epoxide in competition to CO_2 insertion is not part of Figure 9; however, rates of both reactions are not expected to be very different.

Experimental study: In addition to the theoretical study above, a set of experiments was performed with the aim to verify some of the implicit hypotheses of the theoretical study and with the general interest to further understand the action of metal–salen catalysts in the PO/CO_2 copolymerization. The central issues concern synergetic interactions between metal–salen complexes, a multisite catalysis, as discussed for so many transformations involving epoxides and also from the low activation energies of such reactions found in the theoretical part. Emphasis is placed on the chromium– (**1a**) and aluminum–salen (**2**) complexes, mainly differing in Lewis acidity and anion association of the six-coordinate complexes.

A first series of experiments concerned the reactivity of **2**-Cl and epoxide/CO_2.[74] These were carried out in a batch type process in neat PO over 4 h and at 75 °C. Results given are overall results for this reaction period. Formation of polycarbonate is not observed: cyclic propylene carbonate (cPC) is produced exclusively. PO conversion increases about linearly with the amount of activator (Table 4, entries 1–5). The catalysis becomes less than proportionally efficient with CO_2 concentration at higher pressure, 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 (saturated in coordinated epoxide) in a simple bimolecular process. The dependence on the CO_2 pressure is indicative of a slow insertion into the aluminum alkoxide bond that eventually becomes competitive to nu-

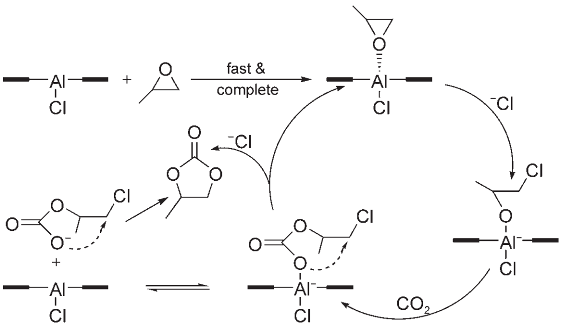
Table 4. Catalysis with salen complexes of Al, Fe, and Zn, and a nucleophilic activator at 75 °C, 4 h reaction time.[a]

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

[a] Extrapolated from a 2 h experiment. Acetate was added as tetraethyl ammonium, chloride as tetrabutyl ammonium salt.

cleophilic attack at higher pressure. Decomposition of the carbonate species apparently is the fastest reaction in the system: chain propagation to yield PPC appears not competitive with the backbiting.

Calculations have shown that the anion de-coordination reaction is particularly easy in aluminum–salen complexes. We want to explain its catalytic action, that is, cPC formation, on account of this ease of de-coordination. Even if small chains were formed, total decomposition of intermediate (poly)carbonato chains would be very efficient as soon as the carbonate anion is liberated from the complex (Scheme 5). Experiments with acetate as external nucleophile and with **2**-OAc as the catalyst gave much lower conversions. The first nucleophilic attack is apparently slow. This is attributed to a smaller polarization and, hence, activation of the epoxide (Table 4) as predicted in the theoretical study.



Scheme 5. Formation of cPC with aluminum–salen and chloride as external nucleophile.

Similar experiments were also performed for [Fe^{III}-(salen)Cl] and [Zn^{II}(salen)] derivatives. Here also the sole formation of cPC was found. The rates for iron–salen are an order of magnitude lower (entries 10, 11). The effective Lewis acidity of this complex is appreciably lower than of aluminum or chromium and was not considered further in this study. Zn–salen complexes catalyze the combination of PO/CO_2 at a rate comparable to aluminum complexes.

A very more complex situation is encountered in the Cr^{III}–salen/nucleophile catalytic system (Table 5). As reported before, the presence of a nucleophile is a prerequisite for the reaction to occur.[35,55,58,65] In general both PPC and cPC are formed. The amount (concentration) of nucleophile has a distinct impact on the product distribution. Increasing the equivalents of nucleophile relative to the salen complex leads to the increased formation of cPC. At a ratio larger than one it becomes the dominant product. This observation is independent of the type of nucleophile, and also of the anion originally in the chromium coordination sphere. There is, however, an influence on rate of PO conversion and also on product ratios (entries 1–6). The PPC formed generally has a carbonate linkage content of over 95 %; however, at low concentration of activator nucleophile, ether linkages are also observed in the range up to 25 %.

The concentration of carbon dioxide and of the catalyst has also a marked impact on the PO conversion. Figure 10 illustrates the effects in case of complex **1a**-OAc with chloride (1 mol equivalent) as activator. The conversion rate is evidently a complex function as it shows a maximum in both dependents.

With respect to CO_2 pressure, it is easily appreciated 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 a favorable condition at about 15 bar of CO_2 pressure and 3000 mol equivalents of PO per catalyst. The pressure dependence at that catalyst concentration is small. Using the combination of a **1a**-Cl and acetate as activator gives somewhat different results with respect to selectivity and a smaller conversion. This illustrates the importance of the starting conditions. A study with various amounts of acetate as nucleophile and the chromium complex **1a**-OAc as catalyst shows the effect of the activator concentration (Figure 11, top, 3000 equiv of PO). The yield of PPC slowly decreases up to a ratio of acetate to chromium of 1:1 with a continuously increasing amount 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 the chromium complex **1a**-Cl and chloride as activator the behavior is similar, but now a clear maximum in the activity and selectivity is observed. The best ratio for PPC formation at 3000 equivalents PO per Cr^{III} was about 0.5, and 1 at 6000 equivalents. It is noticeable that the optimum conditions for polymer for-

Table 5. Converting PO and CO_2 mediated by complex **1a** and nucleophiles at 75 °C. Acetate was added as tetraethyl ammonium, chloride as the tetrabutyl ammonium salt.

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

[a] 91 μmol. [b] 45.5 μmol.

mation are a function of the catalyst concentration; at higher dilution the conversion of PO decreases as well as the selectivity for PPC.

This chromium system **1a**-Cl/chloride was studied in more detail at 65 °C, at which rates are lower (Table 6). Figure 12 (top) shows the dependence of the PO conversion (3000 equivalents of PO and 0.5 mol equivalents of Cl^- to complex **1a**-Cl) and selectivity for PPC with reaction time at 16 bar; the dependence of pressure at 3 h reaction time is shown on the bottom of Figure 12. The catalysis evidently has an induction period in which the selectivity is low for PPC formation. With reaction time progressing, however, PPC becomes the major product. It is (again) observed that 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 behavior is found, again inconsistent with a scheme involving only consecutive reactions at a single catalyst site.

Without detailed mechanistic and kinetic studies and/or starting from several feasible intermediates, a solid proven description of the chromium–salen system cannot be given. However, taking the essentials of the aluminum–salen catalysis, the action of chromium system can be understood if extended with intermolecular chain growth as depicted in Figure 5, and including anion dissociation as the rate-determining step for cPC formation. The following arguments support and illustrate this hypothesis.

The presence of a (more than) stoichiometric amount of nucleophile in the catalysis leads (in due course) to complete conversion of the chromium starting complex to a six-coordinate species, and implies that few coordination sites in the salen complex will be free: the concentration of coordinated (activated) epoxide is relatively low and any bimolecular chain formation is consequential slow. The resulting activity thus resembles that of **2**-Cl, in which M−OC(=O)OR species simply decompose to cPC. Anion dissociation is more extensive at higher dilution, thus better conversions are reached at 3000 than at 1500 mol equivalents of PO, as more epoxide is activated for reaction. Further dilution gives a somewhat lower PO conversion, tentatively 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 carbonato group, formed through an anion dissociation, or by a metal-bound nucleophile. The selectivity for PPC shown in Figure 10 peaks at 3000 equivalents of PO, and can be explained by the increasing concentration of coordinated epoxide with a higher extent of anion dissociation and a lower effectiveness at increasing dilution of bimo-

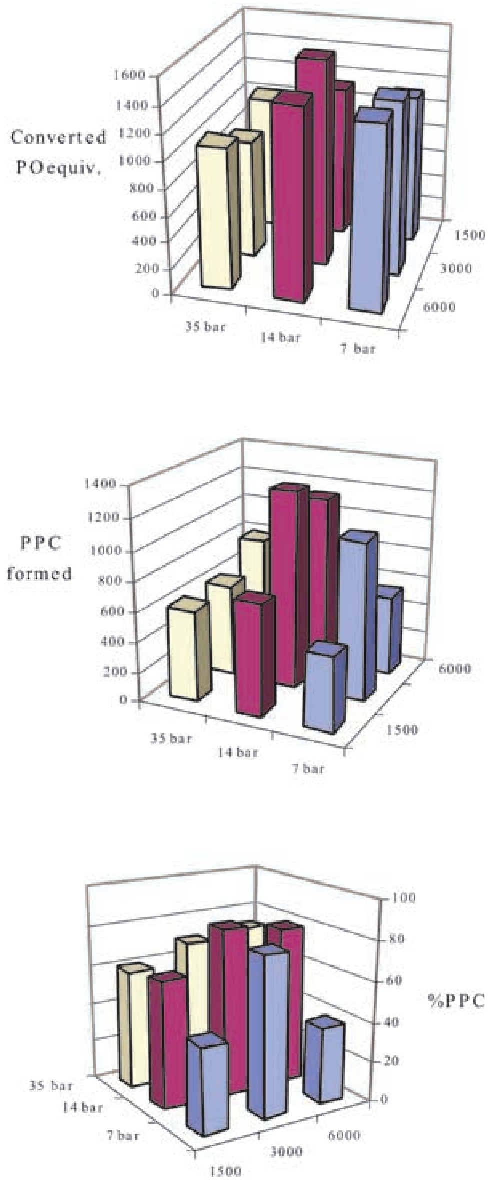


Figure 10. Dependence of PO conversion, PPC formed, and selectivity as function of CO_2 pressure and catalyst concentration (1500, 3000, and 6000 equivalents of PO) at 75 °C using one mole equivalent of tetrabutyl ammonium (TBA) chloride.

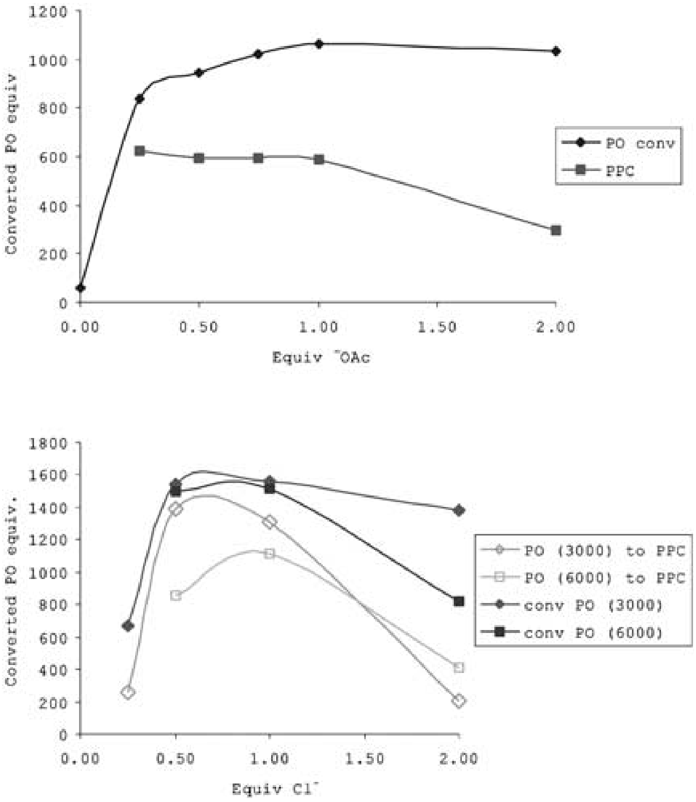


Figure 11. Top: Conversion of PO (3000 equiv) and formation of PPC by using complex **1a**-OAc and tetraethyl ammonium acetate at 75 °C (13 bar of CO_2 pressure and 4 h of reaction time). Bottom: Conversion of PO (3000 equiv) and formation of PPC by using complex **1a**-Cl and tetrabutyl ammonium chloride at 75 °C (14 bar of CO_2 pressure).

Table 6. Converting PO (3000 equiv) and CO_2 mediated by complex **1a**-Cl and TBA chloride (0.5 equiv) at 65 °C, including triplicate results illustrating the limited reproducibility.

	CO_2 [bar]	% PO conversion	Equiv PO in PPC	Equiv PO in cPC	% PPC	*t* [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

lecular reaction with the concomitant decrease at 6000 mol PO per mol Cr.

At high(er) CO_2 pressure both a lower rate of PO conversion and a higher yield of polycarbonate are observed (Figures 9–11). This behavior can be explained by taking the nucleophilicity of five- and six-coordinate [Cr(salen)(carbonate)] complexes into consideration. These species are expected to coordinate in the *trans* position(s) at longer reaction times and at higher pressure, allowing all of the nucleophile initially present, including those in the coordination sphere of chromium, 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 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 salen complex. Propylene carbonate formation is thus more effective in the early phase of the catalysis or at low pressure when strong nucleophilic *trans* ligands induce the liberation of car-

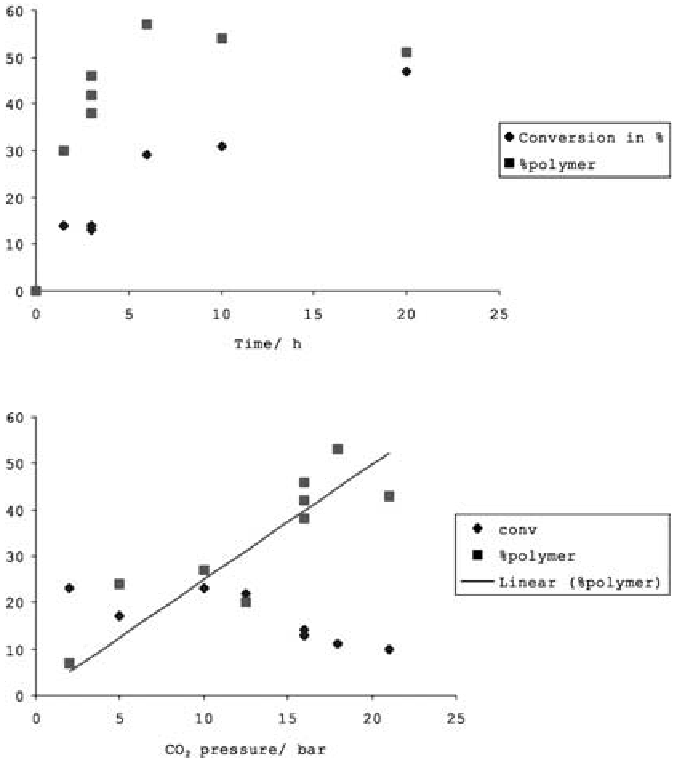
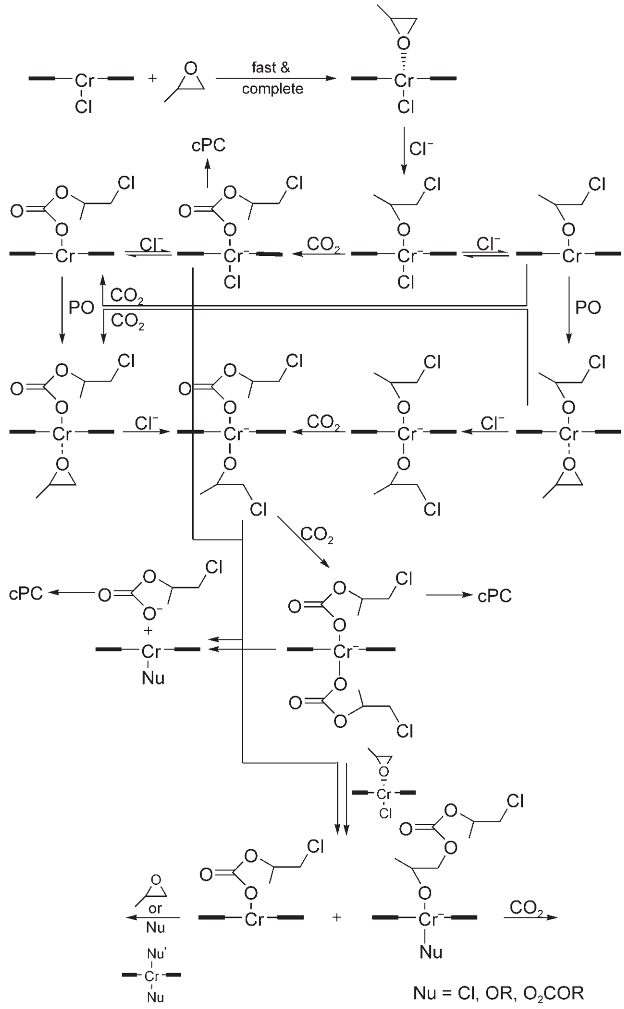


Figure 12. Top: PO conversion and selectivity at 65 °C and pressure of 16 bar CO_2 as function of time. Bottom: PO conversion (3000 mol equiv) with complex **1a**-Cl using 0.5 mol equiv of TBA chloride as activator and 3 h of reaction time.

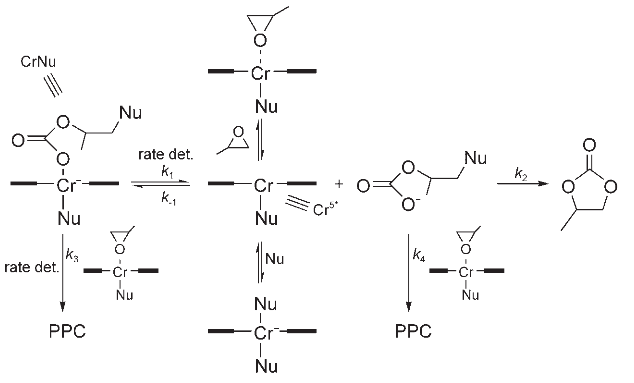
bonato entities. Consistently, Figure 12 shows this dependence as well as the expected limited reproducibility at short reaction times. The catalysis thus is also expected to proceed through an initiation phase to reach a steady state as observed by Darensbourg.[58] Ether linkages in the polymer are particular prominent at high catalyst concentration and low ratios of nucleophile. In those cases, the concentration of coordinated epoxides is relatively high, nucleophilic attack of an alkoxide chromium species becomes competitive to CO_2 insertion, and polyether is formed.

Scheme 6 pertains the catalysis with chromium–salen 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 undergo nucleophilic attack to give negative charged six-coordinate alkoxide complexes. This first anionic compound in the catalytic cycle may insert CO_2 to give a carbonate complex. In addition the exchange of anionic entities is expected to proceed among all chromium species; that is, the chloride atom may decoordinate from the six-coordinate alkoxide chloride complex either in a spontaneous process or through reaction with any five-coordinate chromium–salen complex. The six-coordinate carbonate complex also may be the result of an anion abstraction, CO_2 insertion, and anion coordination reaction sequence. Scheme 6 is thus a simplified depiction of some of the feasible reactions in the system. It indicates the most prominent pathways in the catalytic cycle.



Scheme 6. PO/CO_2 conversion mediated by chromium–salen/nucleophile catalyst system.

In contrast to the aluminum-based conversion of PO and CO_2, anion dissociation is presumed to be much slower and thus becomes the rate-determining step for the formation of cPC. The resting state is accordingly the carbonate complex. Scheme 7 condenses the description of catalytic action into the product (polymer or cyclic carbonate)-determining branching point at the resting state. It is the reactivity of the carbonate species with various *trans* anions (chloride, acetate, or carbonate) that determine the outcome of the catalysis with respect to polycarbonate and cyclic carbonate formation. The importance of the *trans* ligand was recently shown in cobalt–salen systems.[62] If these species effectively react with a coordinated epoxide then polypropylene carbonate results, otherwise decomposition to cPC will eventually occur. The dependence on the CO_2 pressure of the rate and selectivity is related to the nature of the *trans* nucleophile: as its concentration increases, more of the *trans* ligands is transformed into the carbonate group. At the same



$$\frac{d(PO)}{dt} = \frac{d(PPC)}{dt} + \frac{d(cPC)}{dt} \qquad Cr_0 = CrNu_t + Cr\text{-epoxide}_t$$

$$\frac{d(cPC)}{dt} = k_2.[^-O_2COR] = \frac{k_1k_2[CrNu]}{(k_2 + k_{..} + k...)[Cr^{5*}]}$$

$$\frac{d(PPC)}{dt} = (k_3.[CrNu] + k_4^*)[Cr\text{-epoxide}]$$

$$= k_3.[Cr_0][CrNu] - k_3[CrNu]^2 + k_4^*([Cr_0] - [CrNu])$$

assuming that [CrNu] is about $[Nu_0]$ and steady state is reached

$$\frac{d(PPC)}{dt} = k_3.[Cr_0][Nu_0] - k_3[Nu_0]^2 + k_4^*([Cr_0] - [Nu_0])$$

Scheme 7. Essentials of the catalysis by chromium–salen/nucleophile of PO/CO_2 to PPC and cPC.

time the activation/polarization of the epoxide is impacted by the *trans* nucleophile, as the effective Lewis acidity is a function of this parameter. The overall rate of PO conversion is thus in a multiparameter space of several interfering and connecting reactions. As the initial phase is passed a steady state may arise, for which the conversion of PO to PPC is a second-order function of the concentration of nucleophile and a first-order function of the concentration of the chromium–salen complex, with a parabolic maximum at a certain ratio of added nucleophile to salen complex (Scheme 7). This is in accordance with the shape of the observed curves of Figure 11. It also explains the first-order metal complex dependency found by Darensbourg and Chisholm.[58,59]

The above elaboration and data show that a multistep and multicenter catalytic cycle is a feasible and perhaps likely option: it makes the experimental observations explainable. However, the only circumstantial evidence found for multisite chemistry is the parabolic plot for PPC formation and PO conversion, and the polyether microstructures found at high catalyst concentration in combination with low ratios of nucleophile and low CO_2 pressure (and assuming that alkoxide dissociation is not taking place). This last point, however, is only relevant for the formation of polyether from PO.

To further investigate the importance of two-metal-center reactions for the formation of PPC, experiments were performed with mixtures of aluminum– and chromium–salen complexes. The application of a catalyst system based on two different salen complexes would offer the possibility of testing for cooperation, provided that the individual components differ substantially in their individual catalytic actions. The complexes **1** and **2** fulfill this requirement. The results are given in Table 7.

The first entries in Table 7 relate to experiments performed with the **1a**-OAc and **2**-OAc complexes with acetate as the activation agent. Experiments were conducted at 65 and 75 °C. It was found, that the resulting product mixtures are basically determined by the catalytic action of the chromium–salen complex, with a slightly higher ether content in the polymer. This might not be surprising, since the catalytic activity of **2**-OAc complexes in the PO/CO_2 conversion is not particular high.

A further set of experiments was performed at 75 °C, 35 bar overall pressure and 2 h of reaction time and applying aluminum–salen complex **2**-Cl. Effects if at all should show up most prominently in the early phase of reaction and at high(er) concentration of CO_2. Indeed, the product distribution undergoes a change. The formation of PPC is in first approximation independent of the amount of alumi-

Table 7. Crossover experiments with various chromium– and aluminum–salen complexes.

	$n(Cr^{III})$ [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	% PPC	% carb. linkage	T [°C]
	1-OAc	**2**-OAc	OAc^-								
1	45.5		1	14	3000	617	495	120	80	100	65
2		45.5	1	14	3000	120		78			65
3	45.5	45.5	1	14	3000	573	474	99	83	100	65
4	45.5		1	14	3000	1342	1026	300	76	99	75
5		45.5	1	14	3000	75		75			75
6	45.5	45.5	1	14	3000	1833	1413	336	77	95	75
7	45.5		1	35	3000	888	735	153	83	100	75
8		45.5	1	35	3000	99		99			75
9	45.5	45.5	1	35	3000	1311	996	276	76	97	75
	1-OAc	**2**-Cl	Cl^-								
10	45.5	45.5	1	35	3000	714	326	389	46	100	75/2
11	45.5	136.5	1	35	3000	848	323	525	38	100	75/2
12	45.5	0	1	35	3000	582	381	201	65	100	75/2

Table 8. Analysis of the catalysis of PO/CO_2 conversion using mixtures of **1a**-OAc, **2**-Cl, and one equivalent of TBA chloride at 75 °C, 35 bar CO_2 pressure and 2 h of reaction time.

Al^{III} [μmol]	Equiv PO in PPC	M_n (calcd) [gmol^{-1}]	M_n [gmol^{-1}]	Chains/Cr	D (M_w/M_n)	Equiv PO in cPC	Al^{III}-induced cPC formation	%[a] Nu^- at Al^{III}	%[a] Nu^- at Cr^{III}	Calcd equiv PO converted at Cr^{III}	PO converted experimentally
0	381	38862	13400	2.9	1.24	201	201	9	91	688	582
45.5	326	33252	7200	4.6	1.23	389	389	35	65	829	715
136.5	323	32946	5986	5.5	1.22	525	525	48	52	797	848

[a] Theoretical percentage.

num–salen complex; however, the amount of PO converted to cPC increases significantly. This could have various reasons. On the one side, nucleophiles may have reacted with epoxide coordinated to aluminum with consecutive formation of cPC. A simple analysis shows that this is not the case. In the experiment with a threefold excess of **2**-Cl over **1a**-OAc, a minimum of about 30% of the nucleophiles would haven been associated with aluminum (Table 8) to account for the cPC formed. The remaining 70% on chromium, however, should have resulted in much more PPC, as is known from the behavior of **1a**-OAc (Figure 11, bottom). Since this is not observed, processes involving interactions between both species must be considered.

A possibility is that chain ends are transferred from chromium to aluminum, eventually leading to decomposition. In that case, aluminum–salen-related cPC formation should be linearly dependent on its concentration; Figure 13 shows this almost linear dependency. In addition, the quantity of PO converted corresponds within error limits to the amount expected for catalysis by **1a**-OAc in combination with the calculated remaining quantity of nucleophiles associated with chromium (based on a parabolic extrapolation of data of chromium catalysis at 35 bar of CO_2). The total amount of PO transformed was thus activated and attacked at chromium (as function of the average nucleophile binding at the metal center), and formation of cPC occurred by reaction with both **2**-Cl and **1a**-OAc. Consistent with this interpretation, an analysis of the microstructure of the PPC formed by the action of mixtures of chromium– and aluminum–salen complexes shows the same regiochemistry as PPC obtained from chromium–salen alone (ht~76%). This indicates, that polymer formation (epoxide ring-opening) occurs predominantly at chromium; the Lewis acidity has a marked impact on the regiochemistry.[62] Scheme 8 shows the interference of catalysis of **1a**-OAc by **2**-Cl as discussed above.

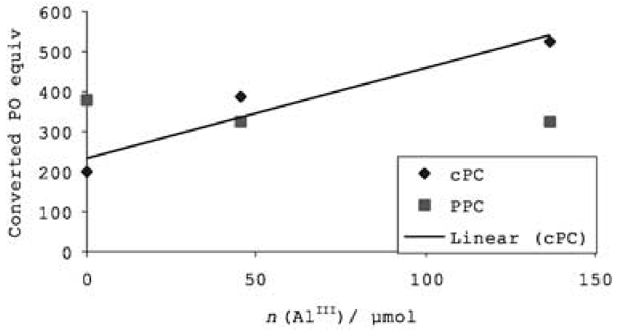
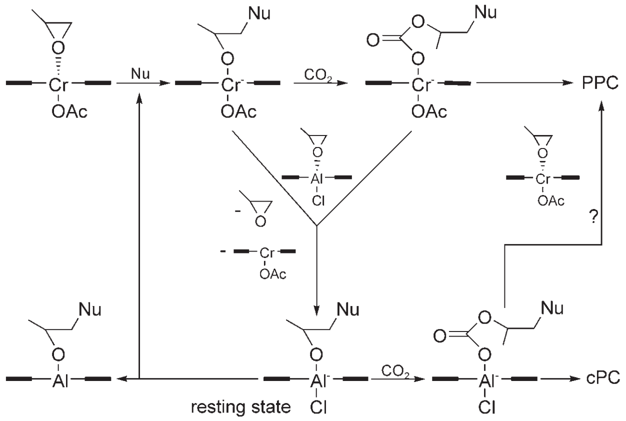


Figure 13. Conversion of PO/CO_2 mediated by mixtures of **1a**-OAc and **2**-Cl at 75 °C, 35 bar CO_2 pressure, and 2 h reaction time.



Scheme 8. Interference of chromium– and aluminum–salen-mediated reactions between PO and CO_2.

If the process in Scheme 8 is the dominant pathway, the molecular weights should also decrease or the distribution broaden as decomposition of the chain end becomes an important pathway. This is indeed observed (Table 8), also as function of the amount of aluminum present. It is found that more chains per chromium are formed, indicative that the chloride nucleophiles that are originally in **2**-Cl also start chains. In this way thus a chain regulation is achieved.

Thus, a consistent picture results: the stronger, more effective Lewis acid **1a**-OAc activates the epoxide for nucleophilic attack and part of the nucleophiles residing at **2** eventually lead to decomposition through anion dissociation in the carbonate. The nucleophiles at aluminum must mainly be in form of the alkoxide, since carbonates are not stable toward dissociation, that is, are more or less unbound to effectively react with chromium-coordinated epoxides and, hence, decreasing the PO rate of conversion. It fits well with the fact that CO_2 insertion is rate-determining for cPC formation mediated by aluminum–salen species.

The remaining question then concerns the mode of nucleophile exchange between **1a** and **2**, either as alkoxide or through nucleophilic attack of chromium carbonate moieties at an aluminum-coordinated epoxide. We favor the latter; however, this is the heart of the matter and remains with circumstantial evidence only.

Concluding Remarks

A DFT study on chromium–salen complexes shows that low energy pathways for an alternating copolymerization of ethylene oxide and carbon dioxide involves 1) coordination of epoxide to a chromium metal, 2) attack of an external nucleophile or a metal-bound carbonate, and 3) direct insertion of carbon dioxide in the metal–alkoxide bond along several low-energy pathways. Copolymerization 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 carbonato chains decomposition is very efficient. Thus anion dissociation and formation of these species during catalysis is essential for the outcome. Anion dissociation is more facile in six-coordinate **2**-Cl complexes than in those of chromium. This should be a factor considered when designing a catalyst with ligand–metal combinations. It may underlie the electronic effects Coates et al.[7] observed with zinc–diketiminate complexes.

The experimental study shows, that the copolymerization of PO and CO_2 mediated by chromium(III)–salen/nucleophile systems have a complex dependence on the concentration and ratios of all the components, with a maximum selectivity for PPC at about 3000 equivalents of PO and 15 bar of CO_2 pressure and an activator amount of less about 0.5 equivalents. The parabolic dependence of the selectivity for PPC 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. In contrast aluminum–salen complexes give only cyclic carbonate. Models are proposed that account for the differences in catalytic action, and include anion dissociation as the rate-determining step in case of chromium and CO_2 insertion for aluminum.

The insights obtained are in accordance with earlier investigations on the copolymerization of PO and CO_2 with an essential role for more than one species. It may be concluded that functional copolymerization systems must fulfill a few prerequisites: 1) the presence of a species that holds a “sufficiently stable” carbonate group that does not undergo dissociation or induce backbiting, 2) a Lewis acid that activates epoxides to such an extent that carbonate nucleophilic attack is feasible, 3) a consecutive thermodynamically favorable carbonate transfer to the epoxide followed by CO_2 insertion, and 4) transfer of the carbonate to the first species. The system becomes simpler if one metal complex can serve all purposes.

Experimental Section

Computational methods: The overall copolymerization reaction involving CO_2 and epoxides was conceptually split into several steps. For each of the steps the corresponding reaction mechanism was investigated by locating the transition state (TS) and the associated reactants and products. The nature of all transition states was verified (only one negative eigenvalue of the hessian). Reactants and products were identified by inducing small distortions in the TS structure along the eigenvector associated with the negative eigenvalue. Distortions with positive and negative amplitude lead to reactants and products after subsequent geometry optimization. All calculations were performed with the quantum-chemistry package TURBOMOLE.[75] DFT methodology was used at the B-P86/SV(P)[76–79] level of theory to locate all stationary points. Single-point energy calculations were carried out by using the TZVP[80] basis set. Geometries were optimized on a 64 processor ATHLON 1800+ Linux cluster and a 64 CPU IBM SP3. The numerical calculation of second derivatives required $6N$ (N = number of atoms) energy and gradient calculations, which were efficiently distributed and carried out in parallel on a network of workstations. This calculation was achieved by using TURBO-SERVER, an in-house development of BASF polymer research, harnessing the power of ordinary NT desktop PCs to carry out quantum chemical calculations “at night”.[81] The effect of solvent was not taken into account.

PO/CO_2 experiments: PO/CO_2 coupling experiments were performed in a 50 or 250 mL steel autoclave equipped with magnetic stirring and external oil bath heating. Prior to reaction, the autoclave was dried at 80 °C under vacuum and kept under inert atmosphere of argon from thereon. During catalytic experiments, the CO_2 pressure was kept constant by using a check valve. CO_2 of purity grade 4.5 was used as provided by BASF Aktiengesellschaft, Ludwigshafen, and was applied in all reactions. PO was obtained from Linde.

Salen complexes were synthesized according to literature preparations starting from 3,5-di-*tert*-butylsalicylaldehyde and 1,2-diaminobenzene and by using chromium(II) chloride,[65] iron(III) chloride,[82] diethyl zinc,[83] or diethyl aluminum chloride[84] as metal precursor.

Conditions for chromium(III)- and aluminum(III)-catalyzed copolymerization experiments: A typical experiment is described. Chromium complex **1a**-OAc (29.6 mg, 45.5 μmol), aluminum complex **2**-Cl (27.4 mg, 45.5 μmol), and tetrabutyl ammonium chloride (12.6 mg, 45.5 μmol) as cocatalyst were transferred into an autoclave (50 mL) followed by 3000 equivalents of propylene oxide (9.6 mL, 137 mmol). The reaction vessel was closed and pressurized with CO_2 to 25 bar. After heating the reactor for 5–10 minutes to 75 °C, the final pressure was adjusted to 35 bar. The autoclave was held for 4 h at 75 °C, after which it was cooled to 10 °C and CO_2 was vented off. Immediately after opening, a sample for ^1H NMR analysis was performed in $CDCl_3$ to determine the product ratio (PPC/cPC) by taking the integral values of the signals at $\delta = 4.9$ and 4.5 ppm. The viscous reaction mixture was subsequently diluted with CH_2Cl_2 and added drop wise to acidified (HCl) methanol resulting in precipitation of polycarbonate. The isolated polycarbonate was dried under vacuum at 60 °C and analyzed by ^1H NMR spectroscopy. The ratio of ether and carbonate linkages were determined from the resonances of the respective methyl groups in between $\delta = 1.2$ and 1.35 ppm.

Experiment addressing the effect of cPC: Complex **1a**-Cl (81 mg, 0.130 mmol) and tetrabutyl ammonium chloride (18 mg, 65 μmol) were dissolved in a mixture of PO (22.6 g, 390 mmol) and cPC (3.4 g, 33 mmol) in a 250 mL autoclave. An initial pressure of CO_2 10 bar was admitted and the autoclave was submerged in an oil bath of 65 °C. After reaching this temperature, the pressure was adjusted to 16 bar and the reaction was run for 3 h. CO_2 was vented of and the ratio of PO/cPC/PPC was deduced from the proton NMR signal intensities to be 760:155:37 (starting ratio PO/cPC was 405:45). From this the conversion of PO was calculated at 12 % (vs 13 % without cPC) and the selectivity for PPC of 36 % (vs 42 % without initial present cPC). This is within error limits.

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