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CO$_2$ Fixation

Salen-Complex-Mediated Formation of Cyclic Carbonates by Cycloaddition of CO$_2$ to Epoxides

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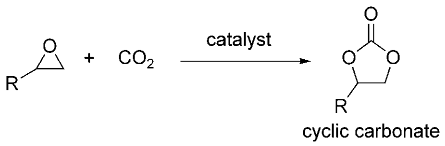
carbon dioxide · cyclic carbonates · epoxides · homogeneous catalysis · salen complexes

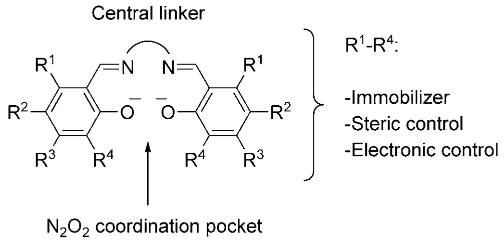
Metal complexes of salen ligands are an important class of compounds, and they have been widely studied in the past. Among their successful catalytic applications, the synthesis of cyclic carbonates by the coupling reaction of epoxides with CO$_2$ has received increased attention; this is mostly due to the importance of using a greenhouse gas as a feedstock for the synthesis of useful molecules. Herein the most relevant past and present research surrounding this topic is presented.

1. Introduction

Concerns about global warming, together with the incoming necessity to find alternative feedstock to fossil fuels, have boosted interest in the use of CO$_2$ as a chemical starting material in recent years.[1] In particular, despite the fact that carbon dioxide is a potential environmental pollutant, its use on an industrial scale for the synthesis of polycarbonates and cyclic carbonates (Scheme 1) represents a much greener alternative to the use of phosgene.[2] Cyclic carbonates are an important class of compounds that can be used as electrolytes in lithium ion batteries, as precursors for pharmaceutical intermediates, raw materials for plastics, and as environmentally friendly nonprotic solvents and degreaser.[3] Cyclic carbonates have been prepared for over 50 years utilizing CO$_2$ as a chemical feedstock,[4] although their preparations often suffered from low catalyst stability and reactivity, air sensitivity, the use of a co-solvent, drastic pressure and temperature conditions, or catalysts based on structures that are not easily accessible. Nevertheless, the last decade has witnessed the development of salen-type ligands (Scheme 2) as scaffolds for the synthesis of more efficient catalysts. Their ease of synthesis was a significant breakthrough towards the development of a catalyst system that can be fine-tuned and potentially employed on an industrial scale, particularly in those cases where chiral cyclic carbonates are pursued or high chemoselectivity for the cyclic carbonate over polycarbonate is needed.



Scheme 1. Cycloaddition of CO$_2$ to epoxides.



Scheme 2. General structure of a symmetrical salen ligand. Substitution on the phenyl rings and linking fragment allows control over the ligand properties.

These salen ligands comprise a N$_2$O$_2$ coordination pocket into which a wide variety of metal ions can be easily accommodated and that function as the catalytic center. Various substituents can be easily introduced in the aromatic rings to allow, for example, control over the approach of a substrate by bulky groups or variation of the Lewis acidity of

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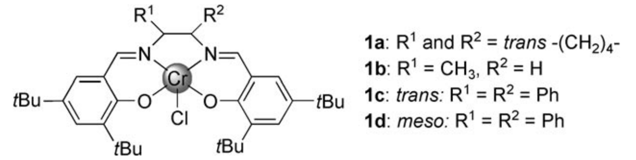
the metal center through electron-withdrawing/donating groups. The insertion of appropriate substituents on the phenyl ring can also be employed to anchor the salen scaffold to a solid support, thus allowing for the preparation of heterogeneous catalysts. Chirality can also be easily introduced in the salen scaffold, either on the phenyl groups or on the backbone bridging fragment. This feature makes this type of catalysts appealing for the synthesis of enantiomerically pure cyclic carbonates using *rac*-epoxides and carbon dioxide.[5] Herein, we discuss the use of metal–salen complexes as homogeneous and heterogeneous catalysts for the coupling reaction of CO_2 and epoxides. Particular emphasis is given to the specific combinations of ligand frameworks, metal ions, and co-catalyst structures that have pushed this research area forward. It is noteworthy that while some of these catalysts are often able to afford both polycarbonates and cyclic carbonates, reaction conditions (for example CO_2 pressure or co-catalyst load) can be tuned to favor the formation of only one desired product. The nature of the substrate employed and the catalytic metal center also play an important role in determining which process will be preferred. This is the case with stronger Lewis acid catalysts, where the formation of cyclic carbonates is usually significantly more relevant.[6] A selection of the most important catalysis results are presented to offer the opportunity to compare various catalytic systems with each other, and also to identify opportunities for further process optimization. Relevant mechanistic work that is considered vital for the development of the next generation of metal–salen catalysts for this highly important class of cyclic carbonate structures is also summarized.

2. Chromium(III)–Salen Complexes

The catalytic formation of cyclic carbonates with chromium complexes was initially accomplished by Kruper and Dellar in 1995, who reported a $Cr^{III/IV}$-tetra-*p*-tolylporphyrinate as a recyclable and very active catalyst for the conversion of oxiranes into cyclic carbonates.[7] In 2001, Paddock and Nguyen changed the coordination environment around the chromium center by using a salen ligand (Scheme 3).[8] The reason behind this choice was the ease of synthesis in comparison to porphyrins and the fact that the condensation of diamine and salicylaldehyde synthons allows the steric and electronic properties of the catalyst to be tuned easily. As for the porphyrin analogue, a Lewis basic co-catalyst, such as 4-dimethylamino-pyridine (DMAP), was employed to carry out the electrophilic addition of CO_2 to epoxides; in the absence of this co-catalyst, no catalytic reaction was observed.



Scheme 3. Cr^{III}–salen complexes for the synthesis of cyclic carbonates from oxiranes.[8]

The variation of the diamine backbone resulted in a prominent change of the catalytic activity. Among the different salen ligands, **1d** has a more accessible coordination site available, which resulted in it being twice as active as the racemic *trans* analogue **1c** (Table 1, entries 1–4). Furthermore, the TOF[9] was greatly increased (Table 1, entries 7–10) upon increase of the ratio of DMAP (up to two equivalents) to a solution of complex **1d**. This catalytic system can operate efficiently at relatively low CO_2 pressures (8 bar) and temperatures (75 °C).

Following these studies, different groups tried to find more advantageous conditions to carry out this transformation. In 2004, García and co-workers decided to study the

Table 1: The coupling reaction of CO_2 and propylene oxide (PO) by complexes **1a–d** under various reaction conditions.[a]

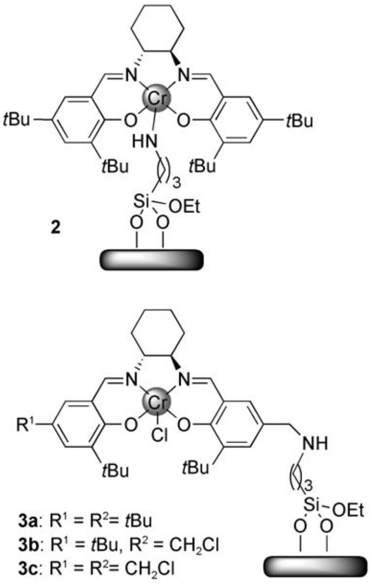
Entry	Catalyst	DMAP equiv	$p(CO_2)$ [bar]	T [°C]	t [h]	TON[b]	TOF[9] [h^{-1}]
1	**1a**	1	7.9	75	2	323	162
2	**1b**	1	7.9	75	2	338	169
3	**1c**	1	7.9	75	2	253	127
4	**1d**	1	7.9	75	2	507	254
5[c]	**1d**	1	7.9	75	2	386	193
6	–	1	11.1	75	2	0	0
7	**1d**	0	11.1	75	2	0	0
8	**1d**	0.5	150	75	2	302	151
9	**1d**	1	11.1	75	2	340	170
10	**1d**	2	11.1	75	2	458	229
11	**1d**	4	11.1	75	2	30	15
12	**1d**	1	7.9	25	14	39	3
13	**1d**	1	7.9	50	7	179	26
14	**1d**	1	7.9	100	1	916	916

[a] Reaction conditions: PO (4 mL, 3.32 g, 5.72×10^{-2} mol), CH_2Cl_2 (0.5 mL), catalyst (0.075 mol%). [b] Mol propylene carbonate produced per mol of catalyst. [c] Reaction carried out in neat PO (4 mL).

Antonello Decortes obtained his MSci from the University of Cagliari (Italy) and his PhD in inorganic chemistry from the University of Nottingham (UK) under the supervision of Prof. Martin Schröder and Dr Jason Love. Subsequently he joined the Institute of Chemical Research of Catalonia (ICIQ) as a postdoctoral researcher, where he is currently working on CO_2 fixation reactions.

Ana M. Castilla studied chemistry at the Universitat de les Illes Balears (Spain) where she completed her PhD in 2008 under the supervision of Prof. Pau Ballester. She is currently working at the Institute of Chemical Research of Catalonia (ICIQ) in Spain, where she is developing multimetallic salen structures for application in homogeneous catalysis.

addition of CO_2 to styrene oxide to form cyclic carbonates under supercritical conditions (100 bar and 80 °C) by dissolving a chromium salen catalyst in an ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate; $bmimPF_6$).[10] These conditions offered the advantage that most of the salen complexes remained dissolved in the ionic liquid during extraction of the reaction product with diethyl ether. However, this route provided only modest conversions ($>50\%$) and product selectivities ($>79\%$). Therefore, to accomplish a more efficient transformation, they attempted a different approach by anchoring the Cr^{III}–salen complex onto a high-surface-area solid support. In these systems, modified amorphous silica and delaminated zeolite ITQ-2 were used. Scheme 4 shows the two different anchoring strategies. In one case, the chromium salen complex was connected to the aminopropylsilyl-modified solid surface (SiO_2 and ITQ-2) through the coordinative, apical bond between a 3-aminopropylsilyl group attached to the solid surface and the chromium ion of the complex (**2** in Scheme 4). A study of the reaction of styrene oxide with CO_2 to form cyclic carbonates under supercritical conditions showed that, although conversion with this system is very high, the catalyst lifetime is dramatically reduced after a first run owing to a high degree of complex detachment. The most effective way of anchoring the chromium complex was through a covalent linkage between the amino fragment of the modified support and one phenolic ring of the salen ligand (**3a–c** in Scheme 4). In this case, the solid particles with the catalyst attached could be simply recovered after the reaction by filtration and reused in consecutive runs after washing in organic solvents without significant loss of the catalytic activity.



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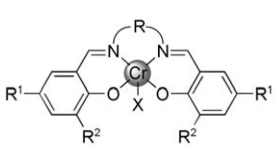
3a: $R^1 = R^2 = tBu$
3b: $R^1 = tBu$, $R^2 = CH_2Cl$
3c: $R^1 = R^2 = CH_2Cl$

Scheme 4. Cr^{III}–salen complexes anchored to a solid support.[10]

Arjan W. Kleij received his MSc and PhD from the University of Utrecht (The Netherlands) working with Gerard van Koten. He then held various postdoctoral and industrial appointments before joining the Institute of Chemical Research of Catalonia (ICIQ) in 2006 as a Group Leader and ICREA fellow. His research interest is in the field of salen chemistry with a focus on new catalytic applications and sustainable chemistry.

Significant contributions to understanding the chemistry of cyclic carbonates came from studies on the co-polymerization of CO_2 with epoxides, where cyclic carbonates are often formed as a by-product. Darensbourg and co-workers dedicated intense studies to the copolymerization of propylene oxide (PO) and carbon dioxide to form poly(propylene carbonate) (PPC) by employing a rich library of [Cr(salen)X] ($X = Cl$, N_3) complexes bearing various electron-donating/withdrawing groups on the diimine backbone (Scheme 5).[6] Their study identified three different available pathways for CO_2/epoxide polymerization process, one of which involves the production of a monomeric cyclic carbonate by-product.[11,12] They observed that the presence of electron-donating groups on the backbone can be used to favor the production of cyclic carbonate with respect to polycarbonate, as is the case for complexes **5** and **6**.

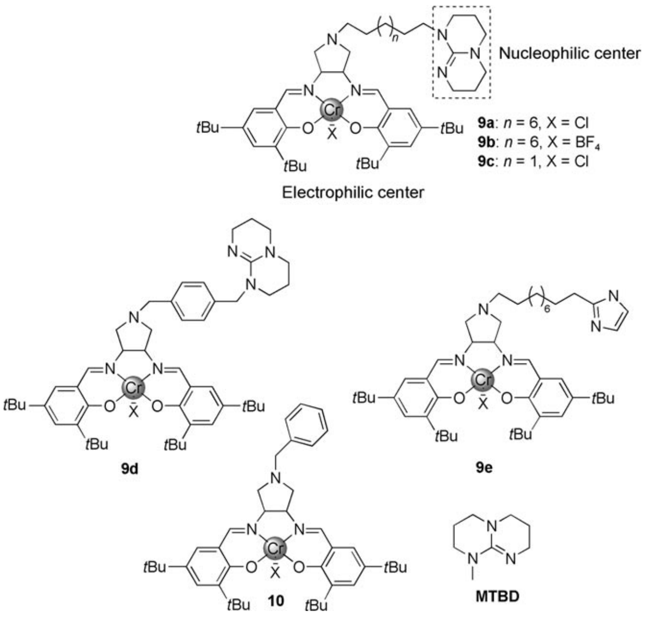


4a: $R = C_6H_4$, $R^1, R^2 = tBu$, $X = Cl$
4b: $R = C_6H_4$, $R^1, R^2 = tBu$, $X = N_3$
4c: $R = C_6H_4$, $R^1 = H$, $R^2 = tBu$, $X = Cl$
5a: $R = c\text{-}C_6H_{10}$, $R^1, R^2 = tBu$, $X = N_3$
5b: $R = c\text{-}C_6H_{10}$, $R^1 = H$, $R^2 = tBu$, $X = N_3$
6a: $R = C_2H_4$, $R^1, R^2 = tBu$, $X = N_3$
6b: $R = C_2H_4$, $R^1 = H$, $R^2 = tBu$, $X = N_3$
7: $R = C_2H_4$ or C_6H_4, $R^1, R^2 = Cl$, $X = N_3$
8: $R = C_2H_4$ or C_6H_4, $R^1 = H$, $R^2 = Ph$, $X = N_3$

Scheme 5. Skeletal representation of the Cr^{III}–salen catalysts used in the co-polymerization of propylene oxide and CO_2.

Nevertheless, the complex containing the electron-withdrawing phenylene diimine backbone (complex **4b**) afforded predominantly copolymer under the same reaction conditions. Their study also highlighted that the electronic effect of the salen ligand on the catalytic activity for polycarbonate production is different for various substrates. In fact, when cyclohexene oxide was used, copolymerization was the favored process when complexes **6** and **7** were employed.

More recently, in 2008, Sun, Lu and co-workers proposed a series of catalysts based on pyrrolidine–Cr^{III}–salen complexes (Scheme 6) comprising an electrophilic center (the Lewis acid metal ion) and a nucleophilic center (a sterically hindered strong organic base).[13] The choice of anchoring a 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) is based on the fact that CO_2 can be activated by bicyclic amidines through the formation of zwitteronic compound, which can add to the epoxide by nucleophilic attack.[14,15] The study of the coupling reaction of CO_2 and propylene oxide using complex **9a** showed that the transformation could be effectively accomplished even at a high [epoxide]/[catalyst] ratio (Table 2, entry 1). This result was in contrast to the activities found for



Scheme 6. Structures of pyrrolidine-based Cr^{III}–salen complexes.[13]

Table 2: The catalyzed reaction of CO_2 and PO under various conditions.[a]

Entry	Catalyst	PO/cat. [mol/mol]	T [°C]	P [bar]	t [h]	TOF[9] [h^{-1}]
1	**9a**	5000	25	5	24	48
2	**10**	5000	25	5	24	<1
3	MTBD	5000	25	5	24	<1
4	**9a**	20000	25	5	24	46
5	**9a**	50000	25	5	24	49
6[b]	**10**/MTBD	5000	25	5	24	<1
7[b]	**10**/MTBD	1000	25	5	24	6
8[b]	**10**/MTBD	500	25	5	24	10
9	**9b**	50000	25	5	24	42
10	**9b**	5000	80	20	1	1819
11	**9c**	5000	25	5	24	42
12	**9c**	5000	80	20	1	2120
13	**9d**	5000	25	5	24	<1
14	**9d**	5000	80	20	1	27
15	**9e**	5000	25	5	24	<1

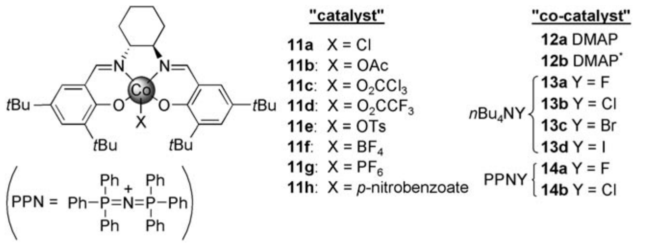
[a] The reaction was performed in neat propylene oxide. [b] Compound **2a**/MTBD = 1:1 (mol/mol).

complex **10** or MTBD separately, which both showed a sharp decrease in activity under the same reaction conditions (Table 2, entries 2, 3). Whilst alteration of the [epoxide]/[catalyst] ratio did not result in any significant change in the activity of complex **9a** (Table 2, entries 4, 5), when the binary catalyst system **10**-MTDA was employed, the reaction rate appeared to be dependent on the catalyst concentration (Table 2, entries 6–8). This result was interpreted as a demonstration that intramolecular two-centered cooperative catalysis of bifunctional units in complex **9a**, where the central metal ion serves as an elecrophilic center and the anchored TBD as a nucleophilic center, is the sole factor for maintaining activity of the catalyst at a high [epoxide]/[catalyst] ratio.

The importance of a synergistic electrophile/nucleophile interaction was further indicated by the result obtained with complex **9d** (Table 2, entries 13, 14) where the *p*-xylylene spacer does not allow for the intramolecular cooperative catalysis observed for the other chromium complexes (**9a–c**). Upon changing the sterically hindered TBD anchored on the pyrrolidine ring of the Cr^{III}–salen complex for a substituted imidazole fragment (**9e**), a significant loss of activity at ambient temperatures was observed. Furthermore, a change in the axial X group of the pyrrolidine–Cr^{III}–salenX complex from Cl to BF_4 did not cause any significant decrease in activity (Table 2, entries 9–12). A possible deactivation mode of the catalyst may involve intramolecular imidazole coordination to the chromium(III) center.

3. Cobalt(III)–Salen Structures

In 1997, Jacobsen and co-workers demonstrated that apart from chromium(III)–salen complexes, the cobalt derivatives also function as catalysts for the ring-opening of epoxides.[16] Prompted by that result, and with the aim of improving the highly efficient Cr^{III}–salen/DMAP catalyst system,[17] Nguyen and co-workers decided to explore the possibility of using cobalt salen complexes as catalysts for the addition of carbon dioxide to epoxides. The coupling of CO_2 with various epoxides catalyzed by Co^{III}–salen complex **11a** (Scheme 7) requires the presence of a Lewis base (LB) as co-catalyst, in the absence of which high activity cannot be reached and only trace amounts of the cyclic carbonate are produced. The activity of the catalytic system was shown to increase with the basicity of the LB and the best catalyst in terms of TOF proved to be **11a**. In this case, two equivalents of co-catalyst (DMAP) were used. Of these two equivalents, one serves as a nucleophile to ring-open the Lewis acid activated epoxide; the second equivalent of DMAP enables the rate-limiting CO_2 insertion step. The reaction of CO_2 and propylene oxide catalyzed by **11a**/DMAP yields propylene oxide with a turnover frequency (TOF) that is comparable to the most active reported (Table 3, entry 1).[18] With this catalytic system (100 °C, 22 bar of CO_2) it was possible to convert a variety of terminal epoxides, such as propylene epoxide, epichlorohydrin, epoxyhexane, (2,3-epoxypropyl)benzene, styrene epoxide, or isobutylene epoxide, into the corresponding cyclic carbonates in near-quantitative yields.[17] Kinetic resolution of



Scheme 7. Binary catalyst systems, consisting of a Co^{III}–salen complex and a co-catalyst, used to promote the addition of CO_2 to epoxides.

Table 3: Enantioselective reaction of CO_2 and propylene oxide.

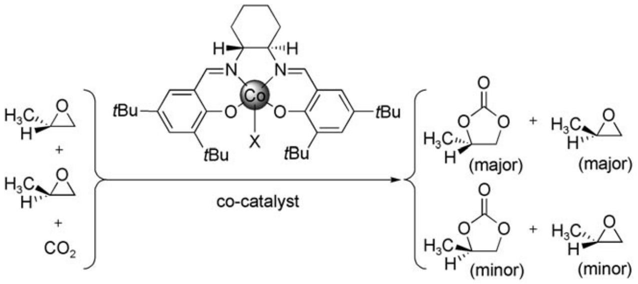
Entry	Cat.	Co-cat.	T [°C]	t [h]	TOF [h^{-1}]	PC yield/*ee* [%]	s[20]
1	**11a**[a]	**12a**	100	0.33	1200	–[d]	1.8
2	**11a**[a]	**12a**	50	8	65	–[d]	2.8
3	**11a**[a]	**12a**	RT	48	9	–[d]	3.0
4	**11a**[a]	**12b**	RT	4.5	115	–[d]	4.8
5	**11a**[a]	**12b**	3	50	10	–[d]	5.6
6	**11b**[b]	**13c**	25	2.5	210	–[d]/42.9	3.9
7	**11c**[b]	**13c**	25	2.0	245	–[d]/50.5	4.8
8	**11c**[b]	**13c**	25	2.0	241	–[d]/51.1	4.8
9	**11d**[b]	**13c**	25	2.2	232	–[d]/46.1	4.3
10	**11a**[b]	**13c**	25	4.0	120	–[d]/39.8	3.3
11	**11e**[b]	**13c**	25	2.5	203	–[d]/51.6	5.2
12	**11b**[b]	**13d**	25	3.0	160	–[d]/37.3	3.0
13	**11b**[b]	**13b**	25	5.5	91	–[d]/54.3	5.7
14	**11e**[b]	**13b**	45	1.5	316	–[d]/35.2	2.8
15	**11e**[b]	**13b**	15	6.0	73	–[d]/63.5	7.2
16	**11e**[b]	**13b**	0	15.0	27	–[d]/70.2	9.0
17	**11f**[c]	**13b**	−10	18	–[d]	4/62	–[d]
18	**11g**[c]	**13b**	−10	18	–[d]	8/59	–[d]
19	**11h**[c]	**13b**	−20	18	–[d]	22/67	–[d]
20	**11e**[c]	**13b**	−20	18	–[d]	15/73	–[d]
21	**11e**[c]	**13a**	−20	18	–[d]	7/77	–[d]
22	**11e**[c]	**13c**	−20	18	–[d]	18/49	–[d]
23	**11e**[c]	**13d**	−20	18	–[d]	23/14	–[d]
24	**11e**[c]	**14b**	−20	18	–[d]	20/73	–[d]
25	**11b**[c]	**14b**	−20	18	–[d]	29/70	–[d]
26	**11d**[c]	**14b**	−20	18	–[d]	35/70	–[d]
27	**11d**[c]	**14a**	−20	18	–[d]	39/75	–d]
28	**11d**[c]	**14a**	−40	120	–[d]	40/83	18.7[d]

[a] Reaction conditions:[17] Cat. (0.066 mol%), co-catalyst (0.132 mol%), PO (3.5 mL, 1500 equiv), CO_2 (22 bar), CH_2Cl_2 (0.5 mL). [b] Reaction conditions:[21] Neat PO (35 mL, 500 mmol), cat. (0.5 mmol, 0.001 equiv), CO_2 (275–300 mmol, 0.55–0.60 equiv, 2–20 bar). [c] Reaction conditions:[22] Neat *rac*-PO (4.38 mL, 62.5 mmol), cat. (0.1 mol%), co-cat. (0.2 mol%), CO_2 (1 bar). [d] Not reported.

racemic propylene oxide was also explored; the best result was obtained using DMAP* (a planar chiral DMAP that has been employed as catalyst in a number of enantioselective reactions)[19] as co-catalyst at 3 °C with a selectivity factor s[20] of 5.6 and a TOF of 10 h^{-1} (Table 3, entry 5).

Almost simultaneously, and also encouraged by the success of Co^{III}–salen complexes as catalysts for the hydrolytic kinetic resolution of epoxides, Lu and co-workers reported a simple and highly efficient chiral Co^{III}–salen/quaternary ammonium halide catalyst system (**11a**–**11e**, Scheme 7) for the kinetic resolution of propylene oxide. This allowed the direct synthesis of optically active cyclic carbonates from *rac*-epoxides (Scheme 8) under extremely mild and solvent-free conditions.[21]

These studies revealed that the quaternary ammonium salt is essential to promote the reaction and has a large effect on the enantiomeric excess and reaction rate (Table 3, entries 6, 12, and 13). Both counterion and temperature also play an important role in the catalytic performance (Table 3, entries 6–11, 14, and 16). At room temperature, the reaction of 0.5 mol of racemic propylene oxide, 0.55–0.60 equiv of CO_2 in the presence of 0.1 mol% of complex **11c** in conjunction with 0.1 mol% of $n$$Bu_4NBr$ as co-catalyst, proceeded within 2 h to afford a mixture of unreacted epoxide and propylene carbonate with moderate enantioselectivity (Table 3, entry 7). The formation rate of propylene carbonate at 25 °C, as expressed in the TOF, reached 245 h^{-1}.

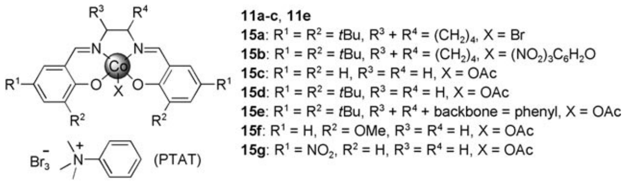


Scheme 8. Kinetic resolution of *rac*-propylene oxide by asymmetric cycloaddition of CO_2 catalyzed by Co^{III}–salen complexes.

Berkessel and co-workers found that the enantioselectivity of this type of catalytic systems (at atmospheric pressure) can be increased by carrying out the reaction at lower temperatures. At −50 °C and an atmospheric pressure of CO_2, the *ee* of propylene carbonate was 87%, with $s = 15.0$, when using the combination **11e**/$n$$Bu_4NCl$ as catalyst.[22] Further studies allowed the discovery of catalytic combinations, giving even better enantioselectivities, albeit with very low conversion rates. The choice of the counterion X turned out to be crucial for the activity of the catalytic system (Table 3, entries 17–19), but not for the enantioselectivity (Table 3, entries 20–23). The screening of several different salts (based on Bu_4N^+ and PPN^+; Scheme 7) revealed that the cation of the organic salt also affects the CO_2 addition (Table 3, entries 24–28). The best result was obtained when **11d** was combined with PPNF at −40 °C, and in this case PC was obtained in 40% yield with 83% *ee* (Table 3, entry 28), which corresponds to a selectivity factor s of 18.7. This work also reported the first preparation of propylene carbonate from propylene oxide and tetrabutylammonium carbonate (TBAMC) with a significantly reduced yield (18%) but again with good enantioselectivity (71% *ee*).

Interestingly, Darensbourg and co-workers showed that an analogous system, where Co^{III} is replaced by a Co^{II} center (that is, Co^{II}–salen/$n$$Bu_4NX$, where $X = Cl$, N_3, Br, I), is very effective in coupling CO_2 and oxetane to provide polycarbonates with a minimal amount of ether linkages.[23] The reaction proceeds via an intermediate, six-membered cyclic carbonate (trimethylene carbonate, TMC) that can undergo in situ ring-opening polymerization to provide the corresponding polycarbonate, poly(TMC), without any loss of its original CO_2 content.

Following the strategy of using a combination of a salen complex and an additive as catalytic system for the chemical fixation of carbon dioxide, Jing and co-workers reported the combination of several Co^{III}–salen complexes with a quaternary onium tribromide compound, namely PTAT (phenyltrimethylammonium tribromide; Scheme 9).[24] The screening of different counterions, frameworks, and substituents (**11a**–**11c**, **11e**, **15a–15g**; Scheme 9) illustrated that the combination **11c**/PTAT is the best catalyst for the addition of carbon dioxide to propylene oxide under extremely mild conditions.



Scheme 9. Co^{II}–salen complexes tested as catalysts in combination with PTAT.[24]

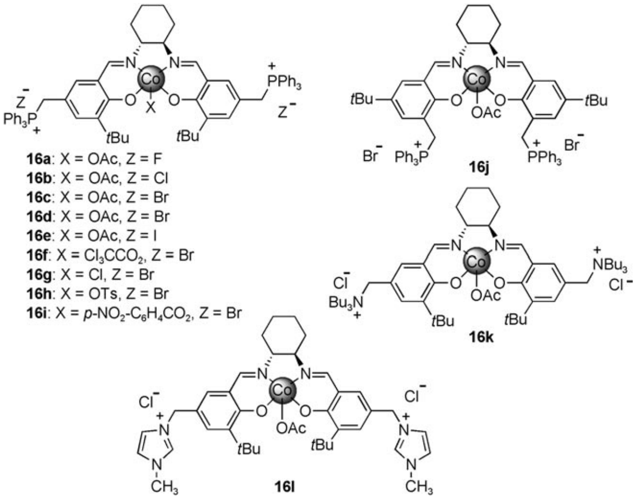
Propylene carbonate was produced in 71 % yield with a TOF value of 706 h^{-1} at 25 °C and 7 bar of CO_2 pressure. The same group also studied the asymmetric version of this type of reaction using a series of chiral catalysts, namely (*R*,*R*)-**11b**, (*R*,*R*)-**11e**, and (*R*,*R*)-**15b** for the coupling reaction of PO and CO_2. Although these catalysts gave low enantioselectivity values (Table 4), they were shown to catalyze the addition of CO_2 to other epoxides, providing good yields and TOF values, with the exception of GMA (glycidyl methacrylate) carbonate, which was obtained in only 29 % yield.

Table 4: The asymmetric coupling reaction of CO_2 and propylene oxide.[a]

Entry	Catalyst	*t* [h]	Yield [%][b]	*ee* [%]
1[c]	(*R*,*R*)-**11b**/TBAB	4	45.1	34.1
2	(*R*,*R*)-**11b**/PTAT	10	57.7	30.2
3	(*R*,*R*)-**15b**/PTAT	15	31.4	45.5
4	(*R*,*R*)-**11e**/PTAT	10	43.1	48.7

[a] Reaction conditions: Co^{III}–salen (0.1 mmol), PTAT (76 mg, 0.2 mmol), epoxide (100 mmol), CO_2 (7 bar); $T = -5$ °C. [b] Yield of isolated product. [c] $T = 25$ °C.

With the aim of preparing chiral cyclic carbonates through the kinetic resolution of racemic epoxides, Jing and co-workers also proposed a series of bifunctional catalysts that combine in one molecule a Lewis acidic metal–salen complex and a quaternary onium salt that supplies a Lewis basic site.[25] The enantioselectivity obtained in the cycloadditon reaction of carbon dioxide to propylene oxide catalyzed by these complexes (**16k** and **16l** in Scheme 10) is of the same magnitude of those previously reported (Table 5, entries 6 and 7).[21,24] Nevertheless, the enantioselectivity was found to increase with the introduction of quaternary phosphonium groups in the salen-type ligands (**16a**–**16e**; Table 5). The screening of different systems resulted in several conclusions: the anion Z of the quaternary onium salt influences both the activity and the enantioselectivity of the reaction (Table 5, entries 1–4 and 8–11). Chloride gives the best *ee* values and iodide the best activities. Variation of the position of the phosphonium group from the 5- to the 3-position in the phenyl side groups also affects the efficiency of the reaction, thereby enhancing the activity but lowering the *ee* (Table 5, entry 5). With respect to the influence of the catalyst counterion, in general acetate gave better enantioselective behavior. However, **16i**, with a *p*-nitrobenzoate group as the counterion, showed a better activity. The best catalyst among the series of complexes screened turned out to be **16b**, which afforded propylene carbonate with 78 % *ee* under extremely mild reaction conditions (0 °C and 6 bar). Unfortunately, when using the same catalytic system for different epoxide substrates, only low to moderate *ee* values were obtained; 9 % *ee* for styrene oxide, 5 % *ee* for phenyl glycidyl ether, 30 % *ee* for epichlorydrin, and 47 % *ee* for 1,2-epoxybutane. It is noteworthy that these catalysts can be recycled five times without significant loss of the activity and enantioselectivity.



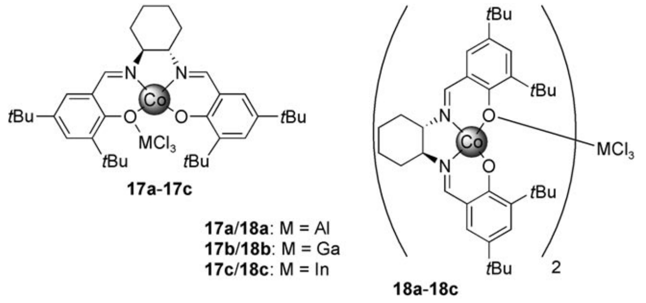
Scheme 10. Bifunctional catalysts.[25]

Table 5: Synthesis of chiral carbonates with catalysts **16a**–**16l**.[a]

Entry	Catalyst	*t* [h]	Conv. [%]	PC *ee* [%]	PC yield [%]	s[20]
1	**16a**	40	14.9	38.3(*S*)	14.7	2.4
2	**16b**	36	29.5	53.1(*S*)	29.4	4.0
3	**16c**	20	44.8	42.0(*S*)	44.7[b]	3.4
4	**16e**	12	53.5	26.3(*S*)	53.5	2.3
5	**16j**	6	43.5	35.0(*S*)	43.4	2.7
6	**16k**	20	26.7	50.2(*S*)	26.5	3.5
7	**16l**	36	31.7	29.1(*S*)	31.6	2.1
8[c]	**16a**	48	8.8	58.2(*S*)	8.6	4.0
9[c]	**16b**	48	23.6	77.8(*S*)	23.5	10.1
10[c]	**16c**	48	36.6	57.0(*S*)	36.5	5.0
11[c]	**16e**	12	33.5	38.7(*S*)	33.3	2.7
12[c]	**16k**	60	9.5	67.7(*S*)	9.3	5.6
13[c]	**16l**	72	8.9	55.5(*S*)	8.9	3.7

[a] Reaction conditions, unless otherwise stated: Catalyst (0.1 mol), PO (100 mmol), CO_2 (6 bar), $T = 20$ °C. [b] The *ee* value (32.1 %) of the remaining PO was also determined. [c] $T = 0$ °C.

Kim and co-workers reported a different approach to improve the enantioselectivity in the coupling reaction of epoxides and carbon dioxide.[26] Chiral Co^{II}–salen complexes can efficiently catalyze these reactions in the presence of a catalytic amount of alkali metal salts, quaternary ammonium halides, or ionic liquids (**17a–c** and **18a–c**; Scheme 11). Mononuclear catalyst **17a** was identified as the most effective among the series used for the insertion of carbon dioxide into propylene oxide, at a CO_2 pressure of 5 bar at room temperature, giving 85 % *ee* when using a catalyst loading of 0.05 % (Table 6, entry 4). The enantiomeric excess of the product was increased by decreasing the loading of the catalyst or by addition of an inorganic base (Table 6). The use of KOH, K_2CO_3, or $KHCO_3$ proved to be effective in improving the *ee*



Scheme 11. Chiral Co^{II}–salen complexes.[26]

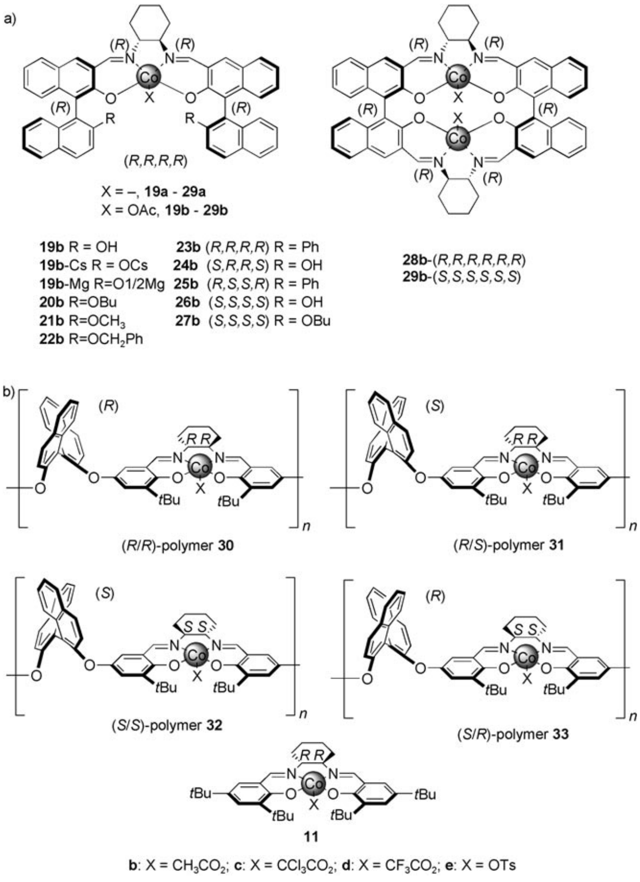
Table 6: CO_2 coupling reaction with racemic propylene oxide.[a]

Entry	Cat.	Co-cat.	Mol ratio[b]	PC *ee*/yield [%]	s[20]
1	**11 b**	–	1:0.005:0	27.3/4.9	1.8
2	**17 a**	–	1:0.005:0	70.3/19.6	6.8
3	**17 a**	–	1:0.001:0	81.0/11.3	10.5
4	**17 a**	–	1:0.0005:0	84.7/8.7	13.1
5	**18 a**	–	1:0.005:0	67.8/19.3	6.1
6	**17 b**	–	1:0.005:0	66.1/17.5	5.6
7	**18 b**	–	1:0.005:0	66.4/18.8	5.7
8	**17 c**	–	1:0.005:0	64.8/17.8	5.4
9	**18 c**	–	1:0.005:0	66.5/18.3	5.7
10	**17 a**	K_2CO_3	1:0.001:0.05	81.6/21.6	12.3
11	**17 a**	$KHCO_3$	1:0.001:0.05	80.9/16.8	11.1
12	**17 a**	KOH	1:0.001:0.05	83.7/23.6	14.5
13[c]	**17 a**	[EMIm]OH	1:0.001:0.0001	74.8/43.2	12.2
14[c]	**17 a**	[EMIm]OH	1:0.0005:0.0005	78.8/39.8	8.0
15[d]	**17 a**	[BMIm]OH	1:0.001:0.0001	83.2/45.1	15.7
16	**17 a**	nBu$_4$NOH	1:0.0005:0.0005	75.0/45.5	10.6

[a] Reaction conditions: PO, CO_2 (5 bar), $T = 25\,°C$, reaction time: entry 2 4 h; entries 1, 5–9, 13–16 3 h; entries 3, 4, 10–12 5 h. [b] Mol ratio PO/cat/co-cat. [c] [EMIm]OH = 1-ethyl-3-methylimidazolium hydroxide. [d] [BMIm]OH = 1-butyl-3-methylimidazolium hydroxide.

values of the resultant propylene carbonate (Table 6, entries 10–12), but the yield was only moderately improved. The yield could also be enhanced by addition of a catalytic amount of quaternary ammonium halides or ionic liquids (Table 6, entries 13–16); both the anion and cation of these co-catalysts have an important effect on the catalytic performance. The use of cations such as EMIm, BMIm, or nBu$_4$N effectively increases the reaction rates, whilst the use of a simple anion such as OH also affords good enantioselectivity.

Jing and co-workers have used the chiral binad–Co^{III} complexes (complexes **19**–**29**; Scheme 12 a) in the presence of PTAT or tetrabutylammonium bromide (TBAB) for the coupling of epoxides and carbon dioxide.[27] These catalysts bear the chiral information both on the bridging fragment and on the binol framework, and this feature showed to affect the enantioselectivity in the asymmetric cycloaddition reaction. When both units have the same chiral configuration (*S* or *R*), PC with an opposite chirality (*R* or *S*, respectively) was obtained. However, when the configurations of the 1,1′-2-binaphthol and 1,2-cyclohexanediamine groups were different (as in **24 b** and **25 b**), the catalyst activity and enantioselectivity decreased. Catalysts with more bulky substituted groups (**20 b**–**23 b**) gave higher *ee* and higher *s* values. Low temperatures were found to favor catalytic abilities and enantioselectivity for the synthesis of chiral PC. The catalyst/co-catalyst combinations **20 b**/PTAT and **27 b**/TBAB were the best catalytic systems under optimized conditions (0 °C and 5 bar of CO_2), thus providing PC with *ee* values of 87 and 84 % and *s* values of 18 and 14, respectively.

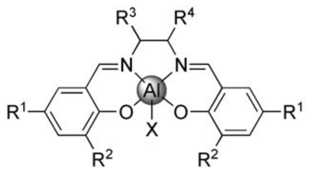


Scheme 12. a) Binad–Co^{III} complexes;[27] b) polymer catalysts based on a binol–Co^{III}–salen complex and the monometallic Co^{III}–salen catalyst **11**.[28]

To increase the *ee* values whilst keeping good catalytic activity, Jing and co-workers also developed four new polymeric binol-based Co^{III}–salen catalysts (**30**–**33**; Scheme 12 b).[28] These systems have an auxiliary chiral site and provide higher enantioselectivity values compared to the traditional Co^{III}–salen catalysts (**11**; Scheme 12 b). The catalytic performance of these systems was examined for the asymmetric cycloaddition of CO_2 to PO at 25 °C and 12 bar. Catalysts comprising the binol and salen units with the same chiral configuration (**30** and **32**) gave (*S*)-PC and (*R*)-PC with moderate *ee* values of 49.2 and 48.2 %, respectively. When the catalysts with opposite configurations were used (**31** and **33**), propylene carbonate with the same chiral configuration as the one in the salen ligand backbone was obtained and with a higher *ee* value. Both the co-catalyst and the anion X of the catalyst proved to be important for catalytic efficiency. The best activity was observed in the presence of PTAT, although the use of TBAF gave higher enantioselectivity. A bulky X group in the polymeric chiral catalysts (for example Cl_3CCO_2) was also essential for obtaining a high enantioselectivity in this reaction. The enantioselectivity obtained with complex **31c** (40.2% conversion, 61.2% *ee* (*S*), $s=6.2$) and **33c** (40.2% conversion, 60.2 *ee* (*R*), $s=5.9$) are higher than the results obtained using the monometallic catalyst **11c** (47.2% conversion, 55.8% *ee* (*S*), $s=5.7$). The catalysts **30c** and **32c** (52.0% conversion, 49.5% *ee* (*R*), $s=4.9$) gave lower *ee* values than **11**, showing that the chirality of the binol fragment plays an important role in further increasing the enantioselective induction of the Co^{III}–salen complexes. Finally, the polymeric binol–Co^{III}–salen complexes could also be recovered and repeatedly used without loss of either activity or enantioselectivity.

4. Aluminum(III)–Salen Structures

The first aluminum salen complexes were prepared as early as 1989 by Le Borgne and co-workers, who showed their effectiveness for the living polymerization of epoxides.[29] However, it was not until 2002 that He et al. investigated new applications in catalysis and synthesis with a green approach, thus preferring the use of relatively nontoxic metals such as aluminum and avoiding the use of chlorinated solvents. They initially studied the formation of propylene oxide in a supercritical (sc) carbon dioxide/ethylene oxide mixture by utilizing a set of binary catalysts comprising an aluminum salen complex (**34a**; Scheme 13) with a quaternary ammonium or phosphonium salt. Their preliminary studies revealed that upon using the Al^{III}–salen/nBu$_4$NBr catalyst, the formation of ethylene carbonate (EC) from sc CO_2/ethylene oxide is twice that under 40 bar CO_2 pressure at same temperature (Table 7, entries 1 and 2).[30] This result was attributed to rapid diffusion and high miscibility of ethylene oxide in supercritical carbon dioxide under the conditions employed. It was established that a typical reaction process proceeds from an initial stage where the reactants and catalyst are present as one supercritical phase, but as the reaction proceeds a new separate phase arises in which ethylene carbonate separates on the bottom of the autoclave. They also showed that temperature has a large effect on the catalytic activity of the binary catalyst (Table 7, entry 3).



34a: X = Cl, $R^1 = R^2 = R^3 = R^4 = H$
34b: X = Et, $R^1 = R^2 = R^3 = R^4 = H$
34c: X = Et, $R^1 = t$Bu, $R^2 = R^3 = R^4 = H$
34d: X = Et, $R^1 = R^2 = t$Bu, $R^3 = R^4 = H$
34e: X = Br, $R^1 = R^2 = R^3 = R^4 = H$
34f: X = OMe, $R^1 = R^2 = R^3 = R^4 = H$
34g: X = Et, $R^1 = R^2 = H$, $R^3 = R^4 = -(CH_4)-$
34h: X = Et, $R^1 = R^2 = NO_3$, $R^3 = R^4 = H$

Scheme 13. Al^{III}–salen complexes with varying substitution patterns.

Table 7: The formation rate of EC from a scCO_2/ethylene oxide mixture under various conditions.[a]

Entry	CO_{2n}/EO [mol/mol]	Catalyst[b]	*T* [°C]	TOF[9] [h^{-1}]
1	2	**34a**	110	2220
2	–	**34a**	110	1140
3	2	**34a**	120	3070

[a] Reaction conditions: Catalyst/EO = 1/5000 (mol/mol), $t=1$ h; pressure 15–16 MPa; density of reactants in the autoclave: 0.6 g cm^{-3}. [b] Co-catalyst is nBu$_4$NBr.

In a subsequent study in 2004, Lu and co-workers investigated how cycloaddition of CO_2 to epoxides is affected by varying the substitution on the aromatic rings of the salen ligands and by using as co-catalyst various [18]crown-6-KY ethers bearing different nucleophilic leaving groups Y.[31] As the Al^{III}–salen and [18]crown-6-KY complexes are soluble in neat epoxides, the reactions were carried out without the addition of any organic (co)solvent. They found that five-membered propylene carbonate could be obtained using complex **34b** (Scheme 13) and [18]crown-6-KI with a TOF of 57.9 h^{-1} under very mild conditions (25 °C, 6 bar CO_2; Table 8, entry 1).

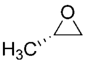
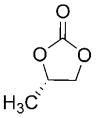
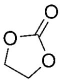
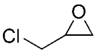
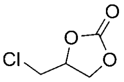
Table 8: Reaction of CO_2 with propylene oxide in the presence of an Al^{III}–salen complex in conjunction with a polyether–KI co-catalyst.[a]

Entry	Al^{III}–salen catalyst	Co-catalyst polyether-KY	TOF[9] [h^{-1}]
1	**34b**	[18]crown-6-KI	57.9
2	**34c**	[18]crown-6-KI	18.4
3	**34d**	[18]crown-6-KI	10.1
4	**34e**	[18]crown-6-KI	62.3
5	**34f**	[18]crown-6-KI	59.6
6	**34g**	[18]crown-6-KI	19.3
7	**34b**	[18]crown-6-KBr	56.7
8[b]	**34b**	[18]crown-6-KCl	3.0
9	**34b**	[18]crown-6-KTOs	0.2
10	**34b**	[18]crown-6-KOAc	2.0

[a] Reaction conditions: Al^{III}–salen (2.4×10^{-4} mol), Al^{III}–salen/polyether-KI/epoxide = 1/1/800 (mol ratio), $T=25$ °C, $t=8$ h. [b] CH_3CN was added as co-solvent.

Substitution of the groups on the aromatic ring (**34c**,**d**; Table 8, entries 2 and 3), or the axial group (**34e**,**f**; Table 8, entries 4 and 5) or/and diamine backbone (**34g**, Table 8, entry 6) proved to be important parameters for the design of an efficient catalyst. Complexes **34a**,**b** were the most effective in catalyzing this reaction, and their activities are at least five times higher than that observed for complex **34d** (Table 8, entry 3). This was ascribed to the high electrophilicity and to a more accessible coordination site for the epoxides. The nature of the anion Y in the complex [18]crown-6-KY also significantly affected the activity of the bifunctional catalyst system (Table 8, entries 7–10). Systems involving iodide and bromide displayed the highest activity if compared with anions with inferior leaving-group ability, such as chloride and acetate. Curiously, although tosylate is traditionally a better leaving group, when using [18]crown-6-KOTs, the cycloaddition reaction could not be effectively catalyzed. A comparison with some other substrates was also carried out, and these results are reported in Table 9.

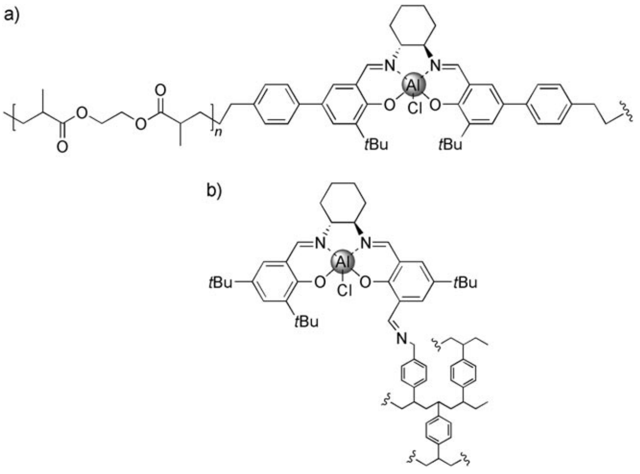
Table 9: The cycloaddition of CO_2 to various epoxides catalyzed by the **34b**/[18]crown-6-KI system.[a]

Substrate	*t* [h]	Product	Yield [%][b]
	12		98
	8		96
	148		95

[a] Reaction conditions: **34b** (16.1 mg, 5×10^{-5} mol), **34b**/[18]crown-6-KI/epoxide = 1/1/400 (mol ratio), $p(CO_2)$ = 6 bar, T = 25 °C; the reaction was carried out in a 10 mL autoclave. [b] Yield of isolated product.

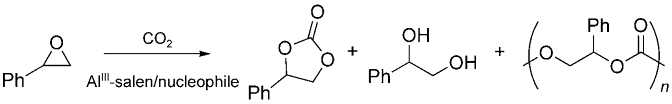
Among the different terminal epoxides investigated (Table 9) and using **34b** as a catalyst, propylene oxide was found to be the most active epoxide, whilst epichlorohydrin exhibited relatively low activity. Notably, the reaction of CO_2 with (*S*)-propylene oxide in the presence of the **34b**/[18]crown-6-KI catalyst system gave (*S*)-propylene carbonate in 98% *ee* with retention of stereochemistry. The activity of complexes **34a–d** and **34h** as catalysts for the formation of propylene carbonate from CO_2 and propylene oxide was again studied in 2004 by combining the bifunctional catalyst systems with quaternary ammonium halides nNBu$_4$X as co-catalyst. This binary system also showed a very efficient conversion at both low temperatures and pressures.[32]

In light of their previous work with Cr^{III}–salen complexes anchored on silica to provide heterogeneous catalysts, in 2005 García and co-workers proposed the use of polymeric Al^{III}–salen complexes in which the backbones consist of a partially cross-linked polystyrene (Al^{III}–salen/PS; Scheme 14b) or poly(ethylene glycol bis-methacrylate) (Al^{III}–salen/PEA; Scheme 14a).[33] The cross-linked poly(styrene-*co*-*p*-divinylbenzene) backbone has pendant amino methyl groups that are useful to covalently attach a salen ligand.



Scheme 14. Polymeric a) Al^{III}–salen/PEA and b) Al^{III}–salen/PS catalysts.

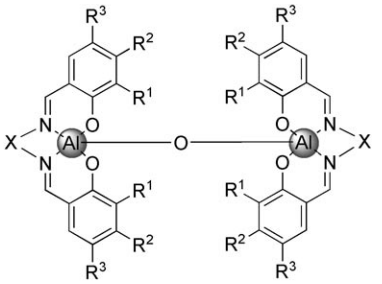
These polystyrene-derived polymers have the disadvantage that the affinity for CO_2 may not be as high as desired, thus the absorption of CO_2 occurs for the most part at the interface between the solid, polymeric catalyst and the liquid phase.[34,35] Therefore, the authors decided to compare the affinity of the above-mentioned polystyrene-supported Al^{III}–salen complex with that of an analogous system that could have a better affinity for CO_2. They envisaged that a polymer containing ethylenedioxy groups could be a suitable candidate to promote a higher local CO_2 concentration.[36,37] For the catalytic studies, the insertion of CO_2 into styrene oxide was used to test the catalytic performance of both types of polymer complexes. To exploit the general miscibility between supercritical carbon dioxide and hydrocarbons, the reactions were carried out in supercritical CO_2 at 80 °C and 100 bar.[38–40] Upon analysis of the reaction mixture by means of GC and IR spectroscopy, they established that in most cases the only product observed was the five-membered cyclic carbonate, although in some of the reactions the corresponding glycol and polycarbonate were also observed (Scheme 15).[41] A comparison of the conversions observed while using the two Al^{III}–salen/PS and Al^{III}–salen/PEA solids showed the latter to give a higher conversion. This result was ascribed to the high oxygen density of the PEA backbone in comparison to the PS polymer support.



Scheme 15. Reaction products observed for the catalytic CO_2 coupling with styrene oxide.

A fine addition to the library of aluminum(III)–salen complexes that are able to perform the conversion of CO_2 and epoxides into cyclic carbonates was provided by North and co-workers. Based on the low environmental impact of aluminum and on previous work on the synthesis of asymmetric cyanohydrins[42] in which they demonstrated that bimetallic salen complexes display a much higher catalytic conversion than their monometallic analogues, they envisioned that a bimetallic Al^{III}–salen complex (Scheme 16) could potentially also display a significantly improved activity in the reaction between carbon dioxide and epoxides.

Complexes **35a–h** were prepared by reacting the salen ligand with aluminum triethoxide, and their dimetallic structure was confirmed by mass spectrometry.[43,44] They were thus used, in combination with nNBu$_4$Br, to catalyze the formation of styrene carbonate from styrene oxide and CO_2. The reaction, which gave no conversion in the absence of either the catalyst or co-catalyst, took place under unprecedented mild conditions (25 °C, 1 atm); the conversion for the different catalysts are summarized in Table 10. The loading of the two components deeply affects the conversion, and increasing the catalyst and co-catalyst load from 0.1 to 2.5 mol% increased the conversion from 5 to 62%. Attempts to improve the catalytic performance were carried out by changing the substitution pattern on the aromatic rings. Of



35a: X = (1*R*, 2*R*)-cyclohexyl, $R^1 = R^3 = t\mathrm{Bu}$, $R^2 = \mathrm{H}$
35b: X = (1*R*, 2*R*)-cyclohexyl, $R^1 = t\mathrm{Bu}$, $R^2 = \mathrm{H}$, $R^3 = \mathrm{NO_2}$
35c: X = $(\mathrm{CH_2})_2$, $R^1 = R^3 = t\mathrm{Bu}$, $R^2 = \mathrm{H}$
35d: X = 1,2-$\mathrm{C_6H_4}$, $R^1 = R^3 = t\mathrm{Bu}$, $R^2 = \mathrm{H}$
35e: X = (1*R*, 2*R*)-cyclohexyl, $R^1 = R^3 = \mathrm{H}$, $R^2 = \mathrm{OMe}$
35f: X = (1*R*, 2*R*)-cyclohexyl, $R^1 = R^2 = R^3 = \mathrm{H}$
35g: X = (1*R*, 2*R*)-cyclohexyl, $R^1 = t\mathrm{Bu}$, $R^2 = R^3 = \mathrm{H}$
35h: X = (1*R*, 2*R*)-cyclohexyl, $R^1 = t\mathrm{Bu}$, $R^2 = \mathrm{H}$, $R^3 = \mathrm{OMe}$

Scheme 16. Structures of dinuclear, O-bridged $\mathrm{Al^{III}}$–salen catalysts **35a–h**.

Table 10: Synthesis of styrene carbonate catalyzed by complexes **35a–h**.[a]

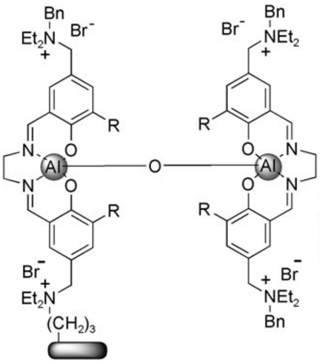
Entry	Catalyst [mol%]	Co-catalyst [mol%]	Conversion[b] [%]
1	**35a** (0.1)	$\mathrm{NBu_4Br}$ (0.1)	5
2	**35a** (2.5)	$\mathrm{NBu_4Br}$ (2.5)	62
3	**35b** (2.5)	$\mathrm{NBu_4Br}$ (2.5)	50
4	**35c** (2.5)	$\mathrm{NBu_4Br}$ (2.5)	52
5	**35d** (2.5)	$\mathrm{NBu_4Br}$ (2.5)	33
6	**35e** (2.5)	$\mathrm{NBu_4Br}$ (2.5)	41
7	**35f** (2.5)	$\mathrm{NBu_4Br}$ (2.5)	28
8	**35g** (2.5)	$\mathrm{NBu_4Br}$ (2.5)	51
9	**35h** (2.5)	$\mathrm{NBu_4Br}$ (2.5)	64

[a] Reaction conditions: $T = 25\,^{\circ}\mathrm{C}$, $p(\mathrm{CO_2})$ 1 bar, reaction time 3 h. [b] Conversions are based on $^1\mathrm{H}$ NMR analysis of the reaction mixture.

the different catalysts that were prepared, none showed significant higher catalytic activity than **35a**. This result was mostly explained by a lower solubility of the other catalysts in neat epoxide rather than to steric or electronic factors. A study was undertaken to test whether different substrates would also show high conversion under the same conditions. Although other terminal epoxides (for example, propylene epoxide) were converted in good yields (up to 77%), disubstituted epoxides were much less reactive, giving poor (*trans*-stilbene oxide, 8%) or no conversion (cyclohexene oxide).

North and co-workers envisioned that the mild conditions under which their system catalyzes the coupling reaction of epoxides and $\mathrm{CO_2}$ could make bimetallic aluminum catalysts very interesting candidates for future industrial applications. Thus, they decided to implement this idea and successfully designed a system in which the catalyst (attached to an organic support material) could be connected to the exhaust stream of a gas flow reactor for the conversion of waste carbon dioxide.[45]

Different silica-based solid supports[46] were selected to be coupled to the bimetallic aluminum catalyst; the systems that were tested are shown in Scheme 17. As an initial step, the catalysts were tested in a batch reactor at room temperature and atmospheric pressure for 20 h using styrene oxide as a substrate. All of the complexes showed good yields in the range 58–78%, with **36d** being the most active. The reusability of the catalyst was also investigated by running a set of 32 sequential reactions under the conditions mentioned above, and a drop of catalytic activity was observed after the first 11 reactions.



36a: R = *t*Bu, support = amorphous silica
36b: R = *t*Bu, support = MCM-41
36c: R = *t*Bu, support = sol-gel
36d: R = H, support = amorphous silica

Scheme 17. Structure of the supported catalysts **36a–d**.

This effect was entirely ascribed to the dequaternization of the catalyst.[47] In fact, full activity was restored by treating the catalyst with benzyl bromide, thus making this system suitable for prolonged uses in a continuous-flow reactor. The system comprises $\mathrm{CO_2}$ and $\mathrm{N_2}$ gas cylinders, which are coupled with a mass-flow controller to supply the gases into the chamber containing the epoxide (ethylene oxide). Experiments were carried out varying the composition in $\mathrm{CO_2}$ of the injection gas, the temperature, and the reaction time, and the results are summarized in Table 11. Among the different catalysts, **36b** was reported to have the highest activity when the reaction was performed at 150 °C. However, at this temperature, a progressive loss of catalytic activity was observed, which was ascribed to demetalation of the catalyst. If the reaction was carried out at 100 °C, the catalyst still retained 50% of its original activity even after seven days. The catalyst could be reactivated by treatment with benzyl bromide, indicating that the loss of activity in this case was due to dequaternization and not to cleavage of the $\mathrm{Al^{III}}$–salen units from the silica support.

5. Other Metal–Salen Structures

In 2003, Shi et al. explored the catalytic performance of copper(II), zinc(II), and cobalt(II) salen-type complexes derived from binaphthyldiamino Schiff bases (Scheme 18) in the chemical fixation of carbon dioxide.[48]

This type of complex was found to efficiently catalyze the formation of cyclic carbonates of terminal epoxides in supercritical $\mathrm{CO_2}$ at 100 °C. The presence of an organic base, such as DMAP (4-dimethylaminopyridine), $\mathrm{Et_3N}$, DBU (1,5-diazabicyclo[5.4.0]undec-5-ene), DABCO (1,4-diazabicyclo-[2.2.2]octane), or pyridine (0.2 mol%), is essential to promote

Table 11: Synthesis of ethylene carbonate in a flow reactor.[a]

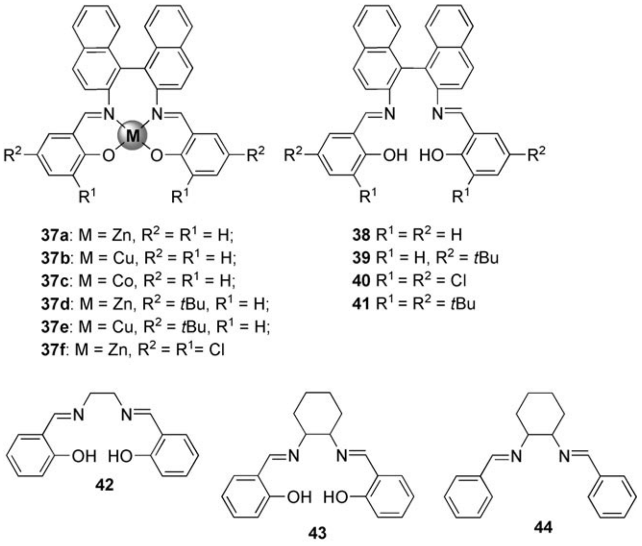
Entry	Catalyst[b]	Reactor *T* [°C]	Reaction *t* [h]	CO_2 reacted [%]	TOF [h^{-1}]
1	**36a**	20	120	6	0.15
2	**36a**	50	19	82	2.2
3	**36a**	60	7	97	2.6
4	**36a**	150	6	57	7.6
5	**36b**	60	7	95	8.3
6	**36b**	60	6	23	8.9
7	**36b**	100	6	54	21
8	**36b**	150	6	66	26
9	**36c**	60	7	97	5.2
10	**36d**	60	7	98	1.1

[a] In each case, the evaporation rate of ethylene oxide was 0.15 mL h^{-1} and the flow rates of CO_2 and N_2 were 1.0 mL min^{-1} and 2.5 mL min^{-1}, respectively, so that the initial composition of the gas stream was 21% ethylene oxide, 25% of CO_2, and 54% N_2. [b] 2.17 g of catalyst were used.

Table 12: Cycloaddtion of CO_2 to PO using various salen-based metal complexes (**37a–f**) or salen ligands (**38–44**).

Entry	Catalyst	Base[b]	*T* [°C]	Yield [%][c]	TON[d]
1	**37a**	DABCO	100	30	30
2	**37a**	Et_3N	100	86	856
3	**37a**	DBU	100	80	803
4	**37a**	DMAP	100	70	702
5	**37a**	pyridine	100	86	833
6	**37b**	DMAP	100	40	397
7	**37c**	DMAP	100	80	800
8	**37d**	DMAP	100	5.3	52.7
9	**37e**	DMAP	100	3	26
10	**37e**	DBU	100	14	141
11	**37f**	DMAP	100	13	132
12[e]	**38**	DMAP	120	89	887
13[e]	**39**	DMAP	120	84	841
14[e]	**40**	DMAP	120	89	887
15[e]	**41**	DMAP	120	15	153
16[e]	**42**	DMAP	120	38	382
17[e]	**43**	DMAP	120	84	838
18[e]	**44**	DMAP	120	14	138

[a] Reaction conditions: PO (2.6 g, 4.5×10^{-2} mol), CH_2Cl_2 (5.0 mL), catalyst (4.5×10^{-5} mol). [b] 2.0 equiv of catalyst used. [c] Yield of isolated product. [d] Mol of propylene carbonate produced per mol of catalyst. [e] $ClCH_2CH_2Cl$ (DCE) as solvent, reaction time 48 h.



Scheme 18. Structures of binaphthyldiamino salen-type complexes and ligands **37–41** and salen ligands **42–44**.[48]

the reaction, and the best bases screened were Et_3N and pyridine (Table 12, entries 1–5) at a catalyst loading of 0.1 mol%. In general, the unsubstituted binaphthyldiamino salen-type Zn^{II}, Cu^{II}, and Co^{II} complexes **37a–c** produce PC in higher yields than substituted **37d–f** under similar conditions (Table 12, entries 1–11). Pressure and temperature are key parameters for attaining high catalyst efficiency. The best catalyst system turned out to be the combination of zinc complex **37a** (0.1 mol%) and Et_3N (0.2 mol%), and optimized conditions comprise a reaction temperature of 100 °C under a high pressure of carbon dioxide. Complexes **37a** and **37b** (in the presence of Et_3N) show efficient catalysis under these optimized conditions (100 °C, 35 bar of CO_2), providing other cyclic carbonates, such as propylene, butylene, epichlorohydrin, or phenylethylene carbonates, in high yields (89–100%) with catalyst loadings of up to 1.0 mol%.[48] Importantly, the catalysts used in this process can be recycled at least 10 times while their activity remains unchanged. The asymmetric version of these cycloaddition reactions was also tested with chiral catalysts **37b** and **37e**, but the enantioselectivities obtained were very low. Based on the combined catalysis results and isotope-labeling experiments, Shi and co-workers postulated a new mechanism that is different from that proposed earlier by Nguyen and Paddock.[8]

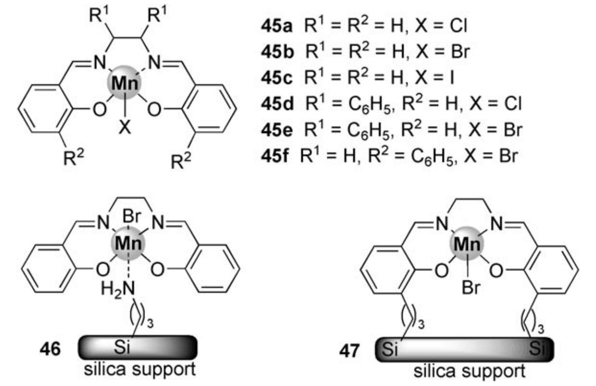
Interestingly, Shi et al. also discovered a unique example of free Schiff bases (**38–44**; Scheme 18) that are able to catalyze CO_2 cycloaddition reactions by themselves, and also in presence of organic bases, such as DMAP, DBU, DABCO, or Et_3N, thus providing cyclic carbonates in excellent yields and under relatively mild conditions.[49] It was found that the presence of both Schiff base (0.1 mol%) and organic base (0.2 mol%) is required to allow the reaction to take place. The use of the organic bases DMAP and DBU provided the best results. The combination of compounds **38–40** or **43** with DMAP gave the carbonate product in high yields (up to 89%) at 120 °C and using 1,2-dichloroethane as solvent.

In contrast, more hindered compound **41** and Schiff-base **42** showed low reactivity. If the Schiff base does not contain phenolic groups, as in the case of compound **44**, the yield of the product is lower under similar conditions. The best reaction conditions were found for Schiff base **38** and DMAP as the co-catalyst at 120 °C under a high pressure of CO_2 (36 bar) with 5 mL of solvent (DCE). Using these conditions, the formation of cyclic carbonates of other epoxides was examined, and again high yields were obtained. It is noteworthy to mention that these catalysts are also recyclable. They can be recovered by distilling off the formed cyclic carbonate and then reused for a subsequent run without loss of catalytic efficiency (Table 12).

Based on these results, which show that hydroxy groups are essential for the reaction to take place, Shi and co-workers tried to simplify the catalytic system by using a combination of phenol (instead of the Schiff base) and an organic base.

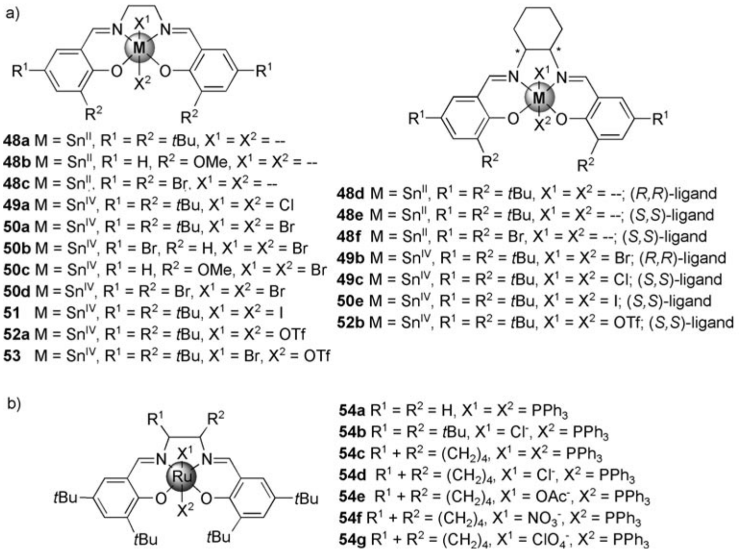
This system also gave good results for the formation of propylene carbonate (98 % yield) by employing a combination of *p*-methoxyphenol (0.4 mol %) with DMAP (0.4 mol %).[49] However, it should be noted that the catalysts summarized in Scheme 18 are generally outperformed by the Cr-, Co-, and Al-salen-based catalysts discussed in Sections 2–4 regarding reaction temperature and pressure.

Jutz, Baiker, and Grunwaldt tested the catalytic activities of a series of homogeneous and heterogeneous Mn^{III}–salen complexes in the cycloaddition of CO$_2$ to propylene and styrene oxides under "solventless" conditions.[50] When using homogeneous complexes (complexes **45a**–**45f**; Scheme 19), the selectivity towards the cyclic carbonate was very high (>99 %). The highest TOFs measured were 213 h^{-1} with catalyst **45c** in the reaction of styrene oxide, and 233 h^{-1} with catalyst **45f** in the reaction of propylene oxide. Both reactions ran without the addition of any solvent or co-catalyst, making their use advantageous with respect to other similar metal–salen systems.[17,26,49,51] Furthermore, manganese salen complexes appear to be more active in these reactions than other Mn^{III} catalysts based on peraza macrocyclic ligands,[52] porphyrins,[53] or manganese–PPN salts.[54] The study of a series of parameters that affect the catalytic performance of these complexes was undertaken. These studies showed that the optimum medium for this reaction is an expanded styrene oxide/CO$_2$ phase which, in presence of the formed carbonate, improves the salen complex solubility and thus enhances its overall catalytic ability. The catalytic activity of Mn^{III}–salen complex **45b** reaches a maximum at 160 °C, and higher reaction temperatures lead to a fast decrease in activity and product yield. This behavior could be influenced by a change in phase distribution of the reactants occurring at higher temperatures, where increasing amounts of styrene oxide are dissolved in the supercritical CO$_2$ phase and less remains in the liquid CO$_2$-expanded phase where the reaction takes place. The amount of CO$_2$ employed in these reactions is also a key parameter. In the reaction of styrene oxide, a maximum in catalytic activity and product yield was achieved when the epoxide/CO$_2$ ratio was close to 1:4, resulting in a two-phase system with a dense, CO$_2$-expanded liquid-like phase and a more gas-like phase on top. When the catalytic activity of the immobilized Mn^{III}–salen compounds was tested in the carbon dioxide addition to styrene oxide, it turned out that compound **46** (Scheme 19), attached to the silica support by coordination through an amine ligand, showed poor catalytic activity despite a very high manganese loading. In contrast, the covalently immobilized catalyst **47** showed better overall performance and reusability, reaching TOFs between 196 and 255 h^{-1}, which are in the range of the homogenous catalyst **45b**. This catalyst is also reusable but requires regeneration by the addition of the halide ligand that is lost during the catalytic reaction.



Scheme 19. Homogeneous and heterogeneous Mn^{III}–salen catalysts used in cyclic carbonate synthesis.

Nguyen and co-workers explored the catalytic performance of tin(II)– and tin(IV)–salen compounds (Scheme 20a) for the preparation of cyclic carbonates by the insertion of carbon dioxide to epoxides as a function of the ligand environment, metal oxidation state, and Lewis acidity.[55] They found that a Lewis base is needed to promote the cycloaddition, and based on their previous work on chromium(III)–salen catalysts for this reaction,[8] they selected DMAP as co-catalyst for these new systems.[17] In the case of Sn^{IV}–salen complexes, the activity of the system is affected by the electronegativity of the axial halogen counterion X. The more electronegative this ligand is, the higher the catalytic activity of the complex, as only one axial ligand is dissociated during the reaction and the remaining axial ligand affects the Lewis acidity of the metal center, and thus the extent to which the epoxides are activated. This hypothesis was supported by the fact that among the catalysts with the same ligand framework (**49a**–**53a**), **53a** gives better activities, having both a bromide as well as a labile triflate as axial ligands. Complex **53a** has a TOF value of 174 h^{-1}, whereas **52a**, bearing two axial triflate ligands, has a value of 29 h^{-1}. Furthermore, complex **50a**, with two axial bromide ligands, has a TOF value of 119 h^{-1}. Electron-withdrawing substitu-



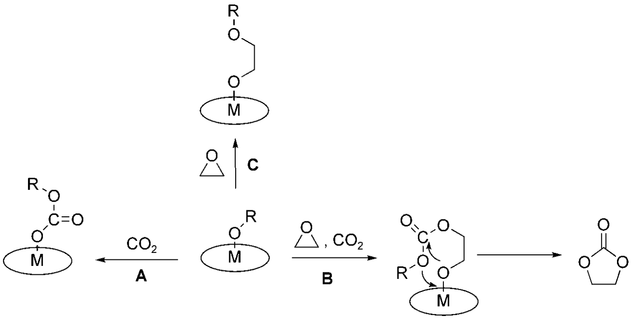
Scheme 20. a) Sn^{II}– and Sn^{IV}–salen catalysts;[55] b) Ru–salen compounds as catalysts for the formation of cyclic carbonates.[56]

ents in the salen ligand framework also increase the catalytic activity, as this causes a higher Lewis acidity of the metal center. Overall, the most efficient catalyst, with two bromide substituents in the salen ligand framework and two axial bromide ligands, was **50 d** with a TOF of 524 h^{-1}. Less Lewis acidic Sn^{II}–salen compounds displayed lower activity than their corresponding Sn^{IV} analogues but followed a similar substituent-dependency trend, with **48 f** (TOF = 190 h^{-1}) being the most active catalyst of the series. Therefore, the activity of these tin complexes is quite respectable, and this system required moderately low CO_2 pressures (8 bar), low catalyst loadings (0.032 mol% relative to PO), and short reaction times (about 4 h), although higher reaction temperatures (120 °C) than for the previously reported chromium(III)–salen systems are required.[8]

Ruthenium salen complexes in conjunction with PTAT have been reported as efficient catalysts for the reaction of carbon dioxide and epoxides.[56] In general, among a series of combinations of Ru^{II} and Ru^{III} complexes with PTAT, EDA (ethyl diazoacetate), TBAB, or DMAP under different conditions, Ru^{III}–salen/PTAT was found to be more effective than catalysts of type Ru^{II}–salen/(EDA or PTAT; Scheme 20 b). Complexes with the ethylene bridging fragment (**54 a** and **54 b**) were better catalysts than those containing the *c*-hexyl bridge (**54 c** and **54 d**). Catalysts systems with TBAB or DMAP gave less effective catalysis, yielding the carbonate in only 50 % and 5 %, respectively. The combination Ru^{III}–salen/PTAT complex **54 b** gave the best results (8 bar of CO_2, 70 °C, no solvent), and furnished the cyclic carbonate in 98 % yield in just 20 min (TOF = 588 h^{-1}). Various cyclic carbonates derived from terminal epoxides were formed in good yields using **54 b** under similar conditions. The lowest yields were obtained with 1,2-disubstituted epoxides, therefore this reaction is controlled by steric effects. These catalysts have potential as recyclable systems, as recycling experiments (5 cycles) showed that the yield of the reaction dropped only slightly from 90 % to 73 %.

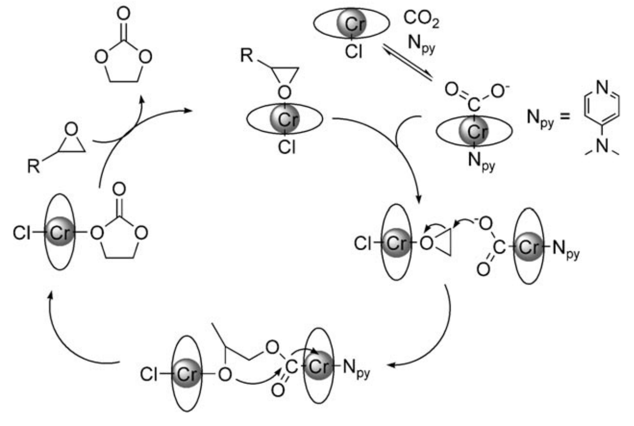
6. Reaction Mechanisms

When CO_2 and an epoxide are catalytically coupled, three different mechanisms can be operative, leading to three different types of product (Scheme 21). After initial coordination of the substrate to the catalyst, formation of a polycarbonate linkage can occur (pathway A). The other alternatives are CO_2 insertion followed by the occurrence of a back-biting mechanism, which results in the formation of a (monomeric) cyclic carbonate (pathway B), or a consecutive epoxide enchainment to afford a polyether linkage (pathway C).[6,11] The three different pathways are influenced by different factors, such as the nature of the substrate, the catalyst and co-catalyst used, and also the reaction pressure and temperature.[57] It is known that at higher temperatures the formation of monomeric cyclic carbonates is normally the favored process. However, when the coupling of CO_2 and epoxides takes place, the occurrence of one specific mechanism is not always exclusive,[12] and therefore to optimize and modulate the production of a specific product (namely monomeric cyclic carbonates), the understanding of the mechanistic details surrounding these reactions is of crucial importance. Various reports on the formation of cyclic carbonates have contributed to show that Lewis base activation of the CO_2 and Lewis acid activation of the epoxide are two crucial steps.[58–60]



Scheme 21. Possible reaction pathways following the coupling reaction of CO_2 with an epoxide.

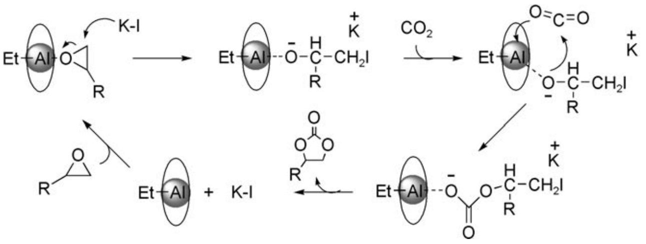
Following the work of Jacobsen and co-workers, who in 1996 clarified that nucleophilic ring opening of epoxides catalyzed by chromium(III) complexes depends on both the electrophilic epoxide and the incoming nucleophile,[61] Nguyen proposed a cooperative bimetallic mechanism involving two different metal species in which their chromium(III)–salen species would fulfill the requirement of activating the epoxide (Scheme 22).[8]



Scheme 22. Proposed mechanism for the cycloaddition of CO_2 to epoxides by a Cr^{III}–salen complex.

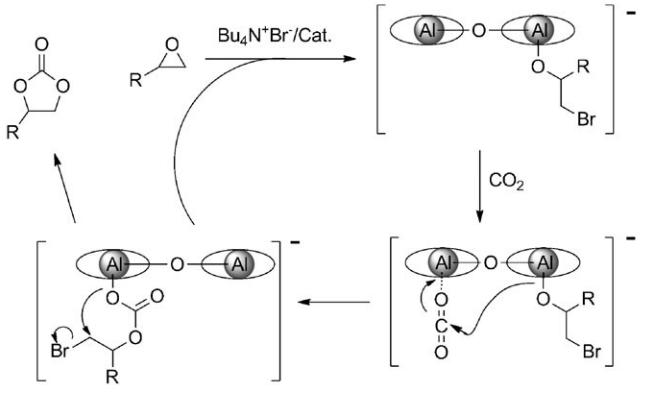
The co-catalyst, in this case DMAP, is essential to form the more electron-rich metal complex Cr^{III}–salen·DMAP. This complex can then activate CO_2, which can further react with an activated epoxide complex at the least sterically hindered carbon. An intermediate is thus formed that will eventually lead to the formation of a five-membered cyclic carbonate. Supporting evidence that the reaction proceeds through this mechanism came from the observation that an increase, beyond optimal concentration, in either DMAP or CO_2 pressure resulted in a dramatic loss in activity. The same mechanism was proposed by Srinivas and co-workers for their Cu^{II}–salen complexes using DMAP as the nucleophile.[62]

Lu and co-workers proposed a monometallic Lewis acid/Lewis base co-catalyzed mechanism for the cycloaddition catalyzed by a mononuclear Al^{III}–salen complex (Scheme 23).[31] Based on the reaction of *trans*-deuteroethene oxide with CO_2, they concluded that the epoxides are ring-opened through the electrophilic interaction of the Al^{III}–salen complex with a synergistic attack of the nucleophile (I) on the less substituted carbon. This is followed by formation of an alcoholate anion that is free to activate CO_2 by attacking its electrophilic carbon atom. Finally, the linear carbonate is transformed into a five-membered cyclic carbonate through an intramolecular elimination step.



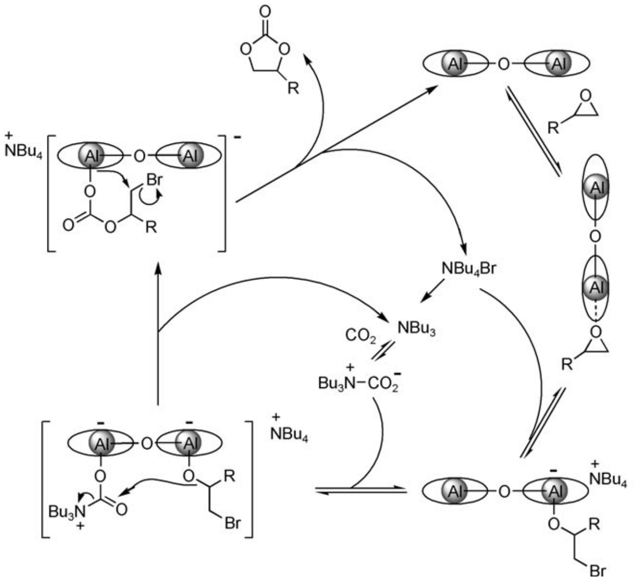
Scheme 23. The Lewis acid/base mechanism proposed by Lu and co-workers.

In the case of the bimetallic $[Al(salen)]_2O$ complexes synthesized by North and co-workers, their structure was thought to be critical from a mechanistic point of view as one of the aluminum centers is proposed to activate the epoxide whilst the other activates a molecule of CO_2.[43] The authors proposed a mechanism in which the epoxide is first ring-opened by attack of the nucleophile, thus affording an aluminum-bound alkoxide (Scheme 24). Carbon dioxide is activated by the second aluminum atom and subsequent intramolecular attack of the alkoxide onto the carbon dioxide gives an aluminum carbonate, which then mediates cyclization and releases the cyclic carbonate product to regenerate both the catalyst and co-catalyst. This reaction pathway was then revisited in 2009 when the authors published a detailed study of the reaction kinetics. Their experiments showed a first-order dependence in substrate and Al^{III}–salen catalyst, but remarkably a second-order dependence in tetrabutylammonium bromide co-catalyst. This result suggested a more prominent role of this component in the rate-determining step of the formation mechanism of the cyclic carbonates. The role of NBu_4Br was investigated by experiments aimed to assess the reusability of the catalyst/co-catalyst system when propylene oxide was used as substrate.



Scheme 24. Possible mechanism to explain the catalytic activity of the bimetallic $[Al(salen)]_2O$ complex synthesized by North and co-workers.

The purity of the propylene carbonate obtained was analyzed by GC and revealed the presence of a second compound, which was identified as tributylamine. Its presence decreased upon reusing the catalysts but was detected again upon further addition of tetrabutylammonium bromide. It was then hypothesized that NBu_4Br was decomposed to tributylamine, with the latter playing an important role in the reaction mechanism. This mechanism was substantiated by kinetic experiments in which different concentrations of $[Al(salen)]_2O$, tetrabutylammonium bromide, and tributylamine were employed, and the experiments showed that the reaction rate depends on all three components. This new-found evidence allowed a new mechanism to be proposed (Scheme 25) where coordination of the epoxide to a Lewis acidic metal center is followed by ring opening by bromide. This intermediate reacts with a carbamate salt molecule (formed by decomposition of a tetrabutylammonium bromide molecule to tributylamine and further reacted with CO_2) to afford a complex in which both the epoxide and the carbon dioxide are activated and pre-organized to mediate an intramolecular coupling. Displacement of a tributylammonium group finally affords a metal-coordinated carbonate, which undergoes subsequent ring-closure to form the cyclic carbonate and regenerates the catalyst. Although to date a limited number of mechanistic investigations have been reported, the details discussed in this section help to explain the catalytic behavior of some metal–salen catalysts in cyclic carbonate formation. This information can facilitate an even



Scheme 25. Catalytic cycle for cyclic carbonate synthesis mediated by a dinuclear Al(salen) complex.

better design of new catalytic systems to overcome selectivity and activity issues.

7. Conclusions and Outlook

Catalytic experiments coupled with mechanistic studies have provided an interesting insight on how metal–salen complexes can be used as efficient catalysts for the coupling reaction of CO_2 with a wide variety of epoxides to ultimately afford five-membered cyclic carbonates. In general, it has emerged that the efficiency of a catalytic system is controlled by various factors, namely the catalytic conditions (CO_2 pressure, temperature, co-solvent used), the electron-donating/withdrawing ability of the substituents on the salen ligands, and obviously the nature of the metal and co-catalyst used. The remarkable progress achieved in the last decade in developing homogenous and heterogenous catalytic systems is a very strong foundation for the development of the next generation of metal–salen catalysts. The general ease and cost-effective synthesis of salen ligands makes the use of these scaffolds very appealing for industrial applications and allows for a beneficial alteration of the catalyst structures by controlling the electronic and steric features or by inserting chiral modules and/or alternative metal ions. Nevertheless, the employment of environmentally more friendly alternatives to potentially toxic metals such as chromium (if oxidized to Cr^{VI}) coupled with mild reaction conditions, a long-lived catalyst, and the avoidance of polluting co-solvents is still a chemical challenge with room for improvement. It is foreseeable that future research will largely have to focus on developing systems aimed at increasing the affinity between the catalyst and both the substrate (for example by increasing the Lewis acidity of the catalytic metal) and CO_2, thus allowing for the employment of milder reaction conditions.[63] These improvements might afford cheap catalysts with unprecedented high catalytic activity that are readily accessible for large-scale industrial applications. It should however be noted that low-temperature processes are not of interest when the synthesis of (cyclic) carbonates is concerned, as effective heat removal from the exothermic reaction offers a way to save energy. The use of metal–salen catalysis should therefore focus on other challenges that involve selectivity issues (see Scheme 21) or new recycling strategies. Another challenge that is still unmet is the efficient and broad-scoped synthesis of chiral cyclic carbonates that are potentially useful as pharmaceutical synthons. In light of their previous success in asymmetric synthesis, the privileged salen ligand (and its complexes) can offer the synthetic community a strong foundation to resolve the above-mentioned issues.

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[1] a) A. Baiker, *Appl. Organomet. Chem.* **2000**, *14*, 751; b) H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults, W. Tumas, *Chem. Rev.* **2001**, *101*, 953; c) M. Aresta, A. Dibenedetto, *Catal. Today* **2004**, *98*, 455; d) I. Omae, *Catal. Today* **2006**, *115*, 33; e) R. Zevenhoven, S. Eloneva, S. Teir, *Catal. Today* **2006**, *115*, 73; f) T. Sakakura, J. C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365; g) M. Aresta, A. Dibenedetto, *Dalton Trans.* **2007**, 2975; h) *Carbon Dioxide as Chemical Feedstock* (Ed.: M. Aresta), Wiley-VCH, Weinheim, **2010**.

[2] For a bibliography on carbonyl chloride (phosgene) and its derivatives, see: a) D. D. Berolzheimer, *J. Ind. Eng. Chem.* **1919**, *11*, 263; b) A. A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951.

[3] a) T. Sakakura, K. Kohno, *Chem. Commun.* **2009**, 1312; b) T. Tokata, Y. Furusho, K. i. Murakawa, T. Endo, H. Matsuoka, T. Hirasa, J. Matsuo, M. Sisido, *J. Am. Chem. Soc.* **1998**, *120*, 4530; c) K. C. Nicolaou, Z. Yang, J. J. Liu, H. Ueno, P. G. Nantermet, R. K. Guy, C. F. Claiborne, J. Renaud, E. A. Couladouros, K. Paulvannan, E. J. Sorensen, *Nature* **1994**, *367*, 630; d) H. T. Chang, K. B. Sharpless, *Tetrahedron Lett.* **1996**, *37*, 3219.

[4] a) M. Lichtenwalter, J. Cooper, U.S. Patent 2,873,282, **1959**; b) W. J. Peppel, *Ind. Eng. Chem.* **1958**, *50*, 767.

[5] J. H. Clements, *Ind. Eng. Chem. Res.* **2003**, *42*, 663.

[6] D. J. Darensbourg, *Chem. Rev.* **2007**, *107*, 2388.

[7] W. J. Kruper, D. D. Dellar, *J. Org. Chem.* **1995**, *60*, 725.

[8] R. L. Paddock, S. T. Nguyen, *J. Am. Chem. Soc.* **2001**, *123*, 11498.

[9] TOF = Turnover frequency: mol product per mol catalyst per hour.

[10] M. Alvaro, C. Baleizao, D. Das, E. Carbonell, H. García, *J. Catal.* **2004**, *228*, 254.

[11] a) D. J. Darensbourg, A. L. Phelps, *Inorg. Chem.* **2005**, *44*, 4622; b) D. J. Darensbourg, P. Bottarelli, J. R. Andreatta, *Macromolecules* **2007**, *40*, 7727.

[12] a) D. J. Darensbourg, J. C. Yarbrough, *J. Am. Chem. Soc.* **2002**, *124*, 6335; b) D. J. Darensbourg, J. C. Yarbrough, C. Ortiz, C. C. Fang, *J. Am. Chem. Soc.* **2003**, *125*, 7586.

[13] X. Zhang, Y.-B. Jia, X.-B. Lu, B. Li, H. Wang, L.-C. Sun, *Tetrahedron Lett.* **2008**, *49*, 6589.

[14] A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartorio, *Tetrahedron Lett.* **2003**, *44*, 2931.

[15] a) E. R. Pérez, M. O. da Silva, V. C. Costa, U. P. Rodrigues-Filho, D. W. Franco, *Tetrahedron Lett.* **2002**, *43*, 4091; b) E. R. Perez, R. H. A. Santos, M. T. P. Gambardella, L. G. M. de Macedo, U. P. Rodrigues-Filho, J.-C. Launay, D. W. Franco, *J. Org. Chem.* **2004**, *69*, 8005.

[16] M. Tokunaga, J. F. Larrow, F. Kakiuchi, E. N. Jacobsen, *Science* **1997**, *277*, 936.

[17] R. L. Paddock, S. T. Nguyen, *Chem. Commun.* **2004**, 1622.

[18] F. Li, C. Xia, L. Xu, W. Sun, G. Chen, *Chem. Commun.* **2003**, 2042.

[19] G. C. Fu, *Acc. Chem. Res.* **2000**, *33*, 412.

[20] The selectivity factor s was determined by using the conversion C and the ee value (expressed as a fraction) of PC product in the equation $s = \ln[1-C(1+ee)]/\ln[1-C(1-ee)]$.

[21] X.-B. Lu, B. Liang, Y.-J. Zhang, Y.-Z. Tian, Y.-M. Wang, C.-X. Bai, H. Wang, R. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 3732.

[22] A. Berkessel, M. Brandenburg, *Org. Lett.* **2006**, *8*, 4401.

[23] D. J. Darensbourg, A. I. Moncada, *Macromolecules* **2009**, *42*, 4063.

[24] T. Chang, H. W. Jing, L. Jin, W. Y. Qiu, *J. Mol. Catal. A* **2007**, *264*, 241.

[25] T. Chang, L. Jin, H. W. Jing, *ChemCatChem* **2009**, *1*, 379.
[26] S. W. Chen, R. B. Kawthekar, G. J. Kim, *Tetrahedron Lett.* **2007**, *48*, 297.
[27] L. Jin, Y. Huang, H. Jing, T. Chang, P. Yan, *Tetrahedron: Asymmetry* **2008**, *19*, 1947.
[28] P. Yan, H. Jing, *Adv. Synth. Catal.* **2009**, *351*, 1325.
[29] a) V. Vincens, A. Le Borgne, N. Spassky, *Makromol. Chem. Rapid.* **1989**, *10*, 623; b) A. Le Borgne, M. Moreau, V. Vincens, *Macromol. Chem. Phys.* **1994**, *195*, 375; c) A. Le Borgne, V. Vincens, M. Jouglard, N. Spassky, *Makromol. Chem. Macromol. Symp.* **1993**, *73*, 37; d) A. Le Borgne, M. Wisniewski, N. Spassky, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1995**, *36*, 217.
[30] a) X. B. Lu, X. J. Feng, R. He, *Appl. Catal. A.* .**2002**, *234*, 25; b) X. B. Lu, R. He, C. X. Bai, *J. Mol. Catal. A* **2002**, *186*, 1.
[31] X. B. Lu, Y. J. Zhang, K. Jin, L. M. Luo, H. Wang, *J. Catal.* **2004**, *227*, 537.
[32] X. B. Lu, Y. J. Zhang, B. Liang, X. Li, H. Wang, *J. Mol. Catal. A* **2004**, *210*, 31.
[33] M. Alvaro, C. Baleizao, E. Carbonell, M. El Ghoul, H. García, B. Gigante, *Tetrahedron* **2005**, *61*, 12131.
[34] X. Han, A. R. Baxter, K. W. Koelling, D. L. Tomasko, L. J. Lee, *Annual Technical Conference-Society of Plastics Engineers* **2002**, *60th*, 1910.
[35] P. Lalanne, S. Rey, F. Cansell, T. Tassaing, M. Besnard, *J. Supercrit. Fluids* **2001**, *19*, 199.
[36] a) K. R. Powell, T. M. McCleskey, W. Tumas, J. M. DeSimone, *Ind. Eng. Chem. Res.* **2001**, *40*, 1301; b) K. Mishima, K. Matsuyama, H. Nagatani, *Fluid Phase Equilib.* **1999**, *161*, 315; c) K. N. West, J. P. Hallett, R. S. Jones, D. Bush, C. L. Liotta, C. A. Eckert, *Ind. Eng. Chem. Res.* **2004**, *43*, 4827; d) R. Fink, D. Hancu, R. Valentine, E. J. Beckman, *J. Phys. Chem. B* **1999**, *103*, 6441.
[37] H. Sellner, J. K. Karjalainen, D. Seebach, *Chem. Eur. J.* **2001**, *7*, 2873.
[38] C. D. Stahl, *Prod. Mon.* **1964**, *22*, 17.
[39] L. W. Holm, V. A. Josendal, *Soc. Pet. Eng. J.* **1982**, *22*, 87.
[40] R. S. Metcalfe, *Soc. Pet. Eng. J.* **1982**, *22*, 219.
[41] D. J. Darensbourg, R. M. Mackiewicz, J. L. Rodgers, C. C. Fang, D. R. Billodeaux, J. H. Reibenspies, *Inorg. Chem.* **2004**, *43*, 6024.
[42] T. R. J. Achard, L. A. Clutterbuck, M. North, *Synlett* **2005**, 1828.
[43] J. Melendez, M. North, R. Pasquale, *Eur. J. Inorg. Chem.* **2007**, 3323.
[44] a) S. J. Dzugan, V. L. Goedken, *Inorg. Chem.* **1986**, *25*, 2858; b) E. P. Balskus, E. N. Jacobsen, *J. Am. Chem. Soc.* **2006**, *128*, 6810; c) D. Rutherford, D. A. Atwood, *Organometallics* **1996**, *15*, 4417; d) Y. Z. Wang, S. Bhandari, S. Parkin, D. A. Atwood, *J. Organomet. Chem.* **2004**, *689*, 759.
[45] M. North, P. Villuendas, C. Young, *Chem. Eur. J.* **2009**, *15*, 11454.
[46] a) T. Soundiressane, S. Selvakumar, S. Menage, O. Hamelin, M. Fontecave, A. P. Singh, *J. Mol. Catal. A* **2007**, *270*, 132; b) L. L. Lou, K. Yu, F. Ding, X. J. Peng, M. M. Dong, C. Zhang, S. X. Liu, *J. Catal.* **2007**, *249*, 102.
[47] a) M. North, R. Pasquale, *Angew. Chem.* **2009**, *121*, 2990; b) M. North, R. Pasquale, *Angew. Chem.* **2009**, *121*, 2990; *Angew. Chem. Int. Ed.* **2009**, *48*, 2946.
[48] Y.-M. Shen, W.-L. Duan, M. Shi, *J. Org. Chem.* **2003**, *68*, 1559.
[49] Y.-M. Shen, W.-L. Duan, M. Shi, *Eur. J. Org. Chem.* **2004**, 3080.
[50] F. Jutz, J.-D. Grunwaldt, A. Baiker, *J. Mol. Catal. A* **2008**, *279*, 94.
[51] a) Ref. [8]; b) S. Yu-Mei, D. Wei-Liang, S. Min, *Adv. Synth. Catal.* **2003**, *345*, 337.
[52] R. Srivastava, T. H. Bennur, D. Srinivas, *J. Mol. Catal. A* **2005**, *226*, 199.
[53] L. Jin, H. Jing, T. Chang, X. Bu, L. Wang, Z. Liu, *J. Mol. Catal. A* **2007**, *261*, 262.
[54] W. N. Sit, S. M. Ng, K. Y. Kwong, C. P. Lau, *J. Org. Chem.* **2005**, *70*, 8583.
[55] H. Jing, S. K. Edulji, J. M. Gibbs, C. L. Stern, H. Zhou, S. T. Nguyen, *Inorg. Chem.* **2004**, *43*, 4315.
[56] H. Jing, T. Chang, L. Jin, M. Wu, W. Qiu, *Catal. Commun.* **2007**, *8*, 1630.
[57] D. J. Darensbourg, R. M. Mackiewicz, D. R. Billodeaux, *Organometallics* **2005**, *24*, 144.
[58] D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.* **1996**, *153*, 155.
[59] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, *J. Am. Chem. Soc.* **1999**, *121*, 4526.
[60] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chem. Commun.* **1997**, 1129.
[61] K. B. Hansen, J. L. Leighton, E. N. Jacobsen, *J. Am. Chem. Soc.* **1996**, *118*, 10924.
[62] R. Srivastava, T. H. Bennur, D. Srinivas, *J. Mol. Catal. A* **2005**, *226*, 199.
[63] A. Decortes, M. Martínez Belmonte, J. Benet-Buchholz, A. W. Kleij, *Chem. Commun.* **2010**, *46*, 4580.