

# Selective Synthesis of Cyclic Carbonate by Salalen Aluminum Complexes and Mechanistic Studies

Mariachiara Cozzolino,<sup>[b]</sup> Tomer Rosen,<sup>[c]</sup> Israel Goldberg,<sup>[c]</sup> Mina Mazzeo<sup>[b]</sup> and Marina Lamberti<sup>\*[a]</sup>

**Abstract:** Salalen aluminum complexes were synthesized and used as catalysts in the reactions of CO<sub>2</sub> with different epoxides. The reaction of cyclohexene oxide and CO<sub>2</sub> was thoroughly investigated. In particular, the effect of the reaction conditions (nature and equivalents of the cocatalyst, CO<sub>2</sub> pressure and temperature) and of the ligands (substituents on the ancillary ligand, nature of the labile ligand and nature of the nitrogen donor atoms) on the outcome of this reaction were studied. The cycloaddition reaction of the CO<sub>2</sub> with terminal epoxides, bearing different functional groups, was realized. Moreover, NMR mechanistic studies allowed to get information on the catalytic cycle. Interestingly, the characterization of an intermediate species in the mechanism of the reaction of cyclohexene oxide with the CO<sub>2</sub>, catalyzed by one of the salalen aluminum complex, was accomplished.

## Introduction

With the increase of world population and the depletion of fossil resources, ensuring a good standard of living to human beings turns to be an ambitious goal. A possible chance is to recover energy and materials from what has been considered, to date, a waste material. Carbon dioxide is the primary source of carbon in life on Earth, however anthropogenic emissions, mainly coming from energy production, industrial processes and transport, have immoderately increased its concentration in the atmosphere, causing serious issues like global warming and ocean acidification. As modern versions of King Midas, the goal of many scientists is to return waste carbon dioxide into valuable chemicals and materials.<sup>[1]</sup> In addition to its abundance, the advantages in the utilization of carbon dioxide as carbon sources include cheapness, non-toxicity and versatility; however its thermodynamic stability is the major impediment. To overcome this issue the reactions with highly energetic molecules, such as hydrogen and epoxides, have been taken into consideration.<sup>[2]</sup> In particular, cyclic carbonates, generated by reaction between epoxides and carbon dioxide, have a

significant commercial interest due to their several uses (i.e. electrolytes in lithium ion batteries, polar aprotic solvents, and intermediates in organic synthesis).<sup>[1b,3]</sup> A number of catalytic systems active in this transformation have been developed with a special attention devoted to complexes deriving from inexpensive and abundant metals, such as aluminium.<sup>[4]</sup> North and co-workers reported bimetallic aluminium salen complexes which are among the most active catalysts for cyclic carbonate synthesis, operating at mild conditions and in cooperation of an onium salt as a cocatalyst.<sup>[5]</sup> Highly active Al-based catalytic systems also include an aluminum triphenolate complex reported by Kleij et al., which efficiently catalyzed reactions of mono- and disubstituted epoxides at 10 bar CO<sub>2</sub> and 70–90 °C in combination with ammonium iodide.<sup>[6]</sup> We recently reported bimetallic salalen-Al complexes which, under proper reaction conditions, were able to selectively produce *cis*-cyclohexene carbonate (*cis*-CHC) and propylene carbonate by reacting CO<sub>2</sub> with cyclohexene oxide and propylene oxide, respectively.<sup>[7]</sup> The comparison of the behaviour of one of these complexes with that of related monometallic half-salen Al complex allowed us to speculate that two metal centers cooperate for the formation of both the polycarbonate and *trans*-CHC while the formation of *cis*-CHC involves a single aluminum center. In this paper, we describe a study in depth of the behaviour of monometallic salalen Al complexes in the CO<sub>2</sub>/epoxide reaction. Moreover, several modifications of the ligand skeleton were realized to study the effect of substituents and the nature of the nitrogen donor atoms on both the selectivity and the activity of the catalysts. NMR mechanistic studies also allowed the characterization of an intermediate of the catalytic cycle.

## Results and Discussion

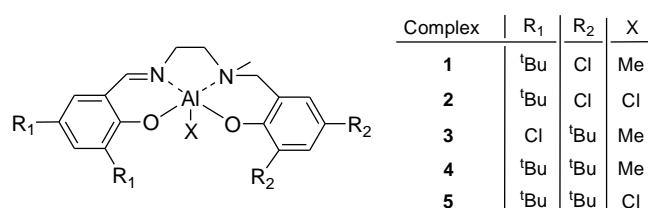
Complexes **1-5** (Scheme 1) were synthesized by reacting the proper salalen precursor ligand with one equivalent of the aluminum precursor, i.e. trimethyl aluminum for complexes **1**, **3** and **4** and dimethylaluminum chloride in the case of complexes **2** and **5**, in benzene at room temperature. Complexes **1-5** were obtained in high yields (78 ÷ 96 %). All complexes were characterized by <sup>1</sup>H, <sup>13</sup>C and COSY NMR spectroscopy. Complexes **3** and **4**, already known in the literature, showed NMR spectra superimposable with those reported.<sup>[8]</sup> The NMR spectra of complexes **1**, **3** and **4** were consistent with the formation of pentacoordinate complexes bearing one salalen ligand and one methyl as labile ligand, which gives a signal at high field (around –0.4 ppm). For complexes **2** and **5** no signal in this region of the spectra was revealed.

[a] Prof. Dr. M. Lamberti  
Department of Physics "E. Caianiello"  
University of Salerno  
Via Giovanni Paolo II, 132  
84084 Fisciano (SA) Italy  
E-mail: mlamberti@unisa.it

[b] M. Cozzolino, Prof. Dr. M. Mazzeo  
Department of Chemistry and Biology "A. Zambelli"  
University of Salerno  
Via Giovanni Paolo II, 132  
84084 Fisciano (SA) Italy

[c] T. Rosen, Prof. Dr. I. Goldberg  
School of Chemistry  
Raymond and Beverly Sackler Faculty of Exact Sciences  
Tel Aviv University  
Ramat Aviv, Tel Aviv 69978, Israel

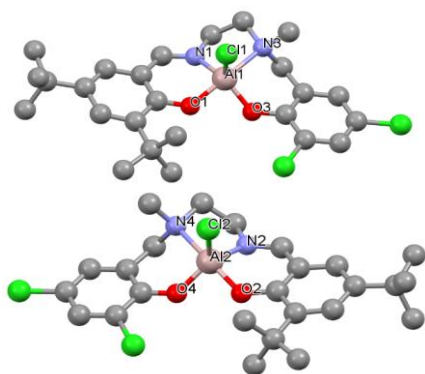
Supporting information for this article is given via a link at the end of the document.



**Scheme 1.** Aluminum complexes 1-5 explored in this work.

As expected, the CH<sub>2</sub> protons of the ligands appear as A<sub>x</sub>B<sub>x</sub> patterns suggesting the coordination of both nitrogen atoms to the metal centre. Complex **2** was also characterized by X-Ray diffraction. The crystals were formed in a solution of the complex in hexane at room temperature. Complex **2** crystallized in space group *P*-1, and the asymmetric unit contains two enantiomeric molecules of the Al-complex (Figure 2) and half a molecule of the solvent (which resides on crystallographic inversion). The structure features a pentacoordinate mononuclear aluminium complex in which all donors of the (ONNO) ligand are bound to the aluminum center. The geometry around Al is closer to square-pyramidal (with Cl at the apical position) than to trigonal-bipyramidal. The bond lengths of the (ONNO) donors to aluminum are unexceptional (Figure 1). Evidently, the Al-N(sp<sup>3</sup>) bonds are considerable longer than the Al-N(sp<sup>2</sup>) ones, as previously observed for similar salalen aluminum complexes.<sup>[8b]</sup> As expected, the phenoxide trans to the imine nitrogen has an Al-O bond distance shorter than that of the phenoxide trans to the amine nitrogen.

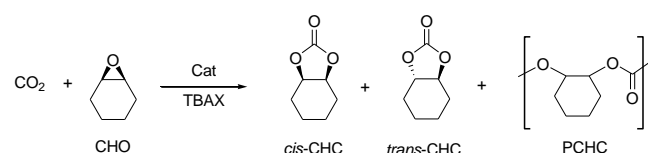
Complexes **1-5** were tested as catalysts in the reaction of CO<sub>2</sub> with cyclohexene oxide (CHO) to test their catalytic activities and product selectivities. The scope of this class of catalytic systems was then expanded by testing complex **1** with several terminal epoxides.



**Figure 1.** Ball-and-stick illustration of the two crystallographically independent molecules of complex **2**. The chirality on N3 is S and on N4 is R. Selected bond lengths (Å): Al1-O1 1.792(2), Al1-O3 1.760(2), Al1-N1 1.949(2), Al1-N3 2.168(2), Al1-Cl1 2.165(1), Al2-O2 1.798(2), Al2-O4 1.755(2), Al2-N2 1.941(2), Al2-N4 2.197(2), Al2-Cl2 2.177(1).

Aluminum complex **1** has been used as catalyst for the CO<sub>2</sub>/CHO reaction in the presence of an onium salt as cocatalyst (Scheme 2). Cyclohexencarbonate was produced as the most abundant product with a selectivity depending on the experimental conditions. The conversion was measured by <sup>1</sup>H NMR spectrum by integrating the signals of the methine protons of the three possible products with respect to the analogue protons of the CHO. The products ratio, that is the reaction selectivity, was determined by means of high resolution NMR spectra.<sup>[7]</sup>

The effect of the experimental conditions (i.e., nature and equivalent of the cocatalyst, structure and loading of the catalyst, temperature and CO<sub>2</sub> pressure) on the outcoming of the reactions has been investigated.



**Scheme 2.** Complexes 1-5 and a quaternary ammonium salt (TBAX) as catalytic systems for the CO<sub>2</sub>/CHO reaction.

In order to avoid solubility problems of the different complexes in the monomer (as some authors report for similar class of complexes<sup>[9]</sup>) we used a minimal amount of methylene chloride to dissolve the complexes and, at the same time, to mix them with the cocatalyst before adding the monomer so playing down the consecutive insertion of the epoxide and thus the formation of the polyether.<sup>[2c]</sup>

Firstly, different cocatalysts were tested in combination with complex **1** by conducting reactions at 30 bar of CO<sub>2</sub> and 80°C. The most abundant product was *cis*-CHC in all cases.

**Table 1.** CO<sub>2</sub>/CHO reaction promoted by complex **1** and onium salts.

Entry <sup>[a]</sup>	Onium salt	Conv (%)	<i>Cis</i> -CHC: <i>trans</i> -CHC:PCHC <sup>[b]</sup>	TON
1	TBAB	28	90 : 2 : 8	328
2	TBAC	16	81 : 3 : 10	187
3	TBAAC	20	84 : 2 : 9	235
4	PPNC	29	88 : 2 : 10	340

[a] General conditions: cat **1** = 42.1 μmol (0.08 mol %), CH<sub>2</sub>Cl<sub>2</sub> = 0.3 mL, CHO = 5 mL (1174 equiv), P<sub>CO<sub>2</sub></sub> = 30 bar, T = 80 °C, time = 20 h.

[b] complement to 100 = polyethers.

The highest conversions were obtained with the PPNC and TBAB. In addition, with this last ammonium salt, the highest value in the percentage of *cis*-CHC was obtained. For this

reason we choose to use TBAB as cocatalyst to study the effect of the reaction conditions and the substrate scope.

By conducting reactions at 30 bar and 80 °C and increasing the equivalents of the cocatalyst, an improvement of the performance of the catalyst in terms of both activity and selectivity was observed (entries 1-4 in Table 2). The increasing in the formation of cyclic carbonate products as a consequence of the presence of an excess of nucleophile has already been observed by other authors.<sup>[2c, 10]</sup> In this case, increasing the equivalents of TBAB, the selectivity versus *cis*-CHC increased, obtaining them as the exclusive product from 4 equivalents of salt.

By raising the temperature, the activity improved (cf entries 4 and 5, Table 2). Lowering the CO<sub>2</sub> pressure, from 30 to 2 bar, had no effect on the product selectivity while the activity decreased by working at 2 bar (cf entries 5, 6 and 7, Table 2). Lastly, by lowering the loading of the catalyst, the highest TOF was obtained at 30 bar and 100 °C (entry 8 in Table 2). Worth noting, in the presence of this class of salalen aluminum complexes, the selectivity of the formation of carbonate linkage was excellent.

With respect to previously reported salalen bimetallic aluminum complexes, these salalen monometallic aluminum complexes show similar catalytic activities but a highest selectivity towards CHC product, this is what we expected on the basis of our previously reported result that the production of polycarbonates involves two metallic centers.

**Table 2.** CO<sub>2</sub>/CHO reaction promoted by complex **1** and tetrabutylammonium bromide (TBAB).<sup>[a]</sup>

Entry <sup>[a]</sup>	TBAB (eq)	P <sub>CO2</sub> (bar)	Temp (°C)	<i>Cis</i> -CHC <sup>[b]</sup>	TON	TOF (h <sup>-1</sup> )
1	1	30	80	91	106	5
2	2	30	80	96	340	17
3	4	30	80	>99	505	25
4	8	30	80	>99	810	40
5	8	30	100	>99	904	45
6	8	10	100	>99	927	46
7	8	2	100	>99	575	29
8 <sup>[c]</sup>	8	30	100	>99	1291	64

[a] General conditions: **1** = 42.1 μmol, CHO = 5 mL (1174 equiv), CH<sub>2</sub>Cl<sub>2</sub> = 0.3 mL, time = 20 h. [b] complement to 100 = PCHC. [c] **1** = 21.05 μmol.

Next, we explored the effect on the outcome of the reaction played by the substituents on the ligand skeleton, the labile ligand and the nature of the nitrogen donor atoms (Table 3). We

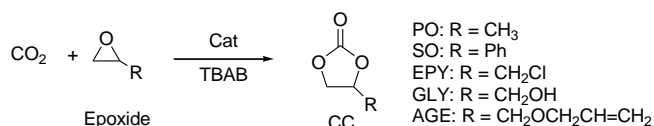
carried out the CHO/CO<sub>2</sub> reactions at 2 bar of CO<sub>2</sub> and at 100 °C, by using complexes **1-5** and 8 equivalents of TBAB. In all cases, *cis*-CHC was obtained as the exclusive product. In general, the effect of the ligands on the conversions was not considerable, however some tendencies can be outlined. First, methyl derivatives gave better conversions with respect to chloride derivatives. Complex **1**, which features halo substituents on the amine-side phenol and bulky alkyl groups on the imine-side phenol, and complex **2**, with the opposite phenolate substitution pattern, showed similar conversion. Whereas complex **4**, bearing *t*-butyl substituents on both sides, resulted less active. This can be explained taking into account that electron withdrawing substituents may increase the Lewis acidity of the aluminum centre, irrespectively of their position.

To evaluate the effect of the nature of the nitrogen atoms in the ligand skeleton, we synthesized aluminum complexes **6**<sup>[11]</sup> and **8**<sup>[12]</sup> bearing, respectively, salen and salan ligands with *t*-butyl substituents in the *ortho* and *para* positions of the phenolate rings and one methyl as labile ligand (see Schemes S2 and S3 in the Supporting Information). The comparison between complexes **4**, **6** and **8**, with the same ligand substitution pattern and the same labile ligands, showed that the most active complex is the salen aluminum species, whereas the salan and salalen complexes gave the same conversion. Likely, the planar conformation of the complex bearing the salen ligand is beneficial in this reaction.<sup>[13]</sup> Complex **7**,<sup>[14]</sup> bearing the same salen ligand of complex **6** but a chlorine as labile ligand,

**Table 3.** Complexes **1-8** and TBAB as catalysts for the CO<sub>2</sub> / CHO reaction.<sup>[a]</sup>

Entry	Cat	Conv (%)	TON	TOF (h <sup>-1</sup> )	
1	<sup>t</sup> BuClAlMe	<b>1</b>	49	575	29
2	<sup>t</sup> BuClAlCl	<b>2</b>	38	399	20
3	Cl <sup>t</sup> BuAlMe	<b>3</b>	47	551	28
4	<sup>t</sup> Bu <sup>t</sup> BuAlMe	<b>4</b>	34	446	22
5	<sup>t</sup> Bu <sup>t</sup> BuAlCl	<b>5</b>	34	446	22
6	salenAlMe	<b>6</b>	48	563	28
7	salenAlCl	<b>7</b>	41	481	24
8	salanAlMe	<b>8</b>	34	446	22

[a] General conditions: cat **1-8** = 42.1 μmol, TBAB = 8 equiv, CH<sub>2</sub>Cl<sub>2</sub> = 0.3 mL, CHO = 50 mmol (5 mL). Temperature = 100°C, P<sub>CO2</sub> = 2 bar, time = 20 h.



**Scheme 3.** Cycloaddition of terminal epoxides and CO<sub>2</sub> promoted by complex **1**.

**Table 4.** Cycloaddition of terminal epoxides and CO<sub>2</sub> promoted by complex **1** and TBAB.

Entry <sup>[a]</sup>	Epoxide R =	Time (h)	Conv (%)	TON	TOF (h <sup>-1</sup> )
1	CH <sub>3</sub>	1	54	1830	1830
2	Ph	5	43	900	180
3	CH <sub>2</sub> Cl	5	86	2612	522
4	CH <sub>2</sub> OH	5	92	3295	659
5	CH <sub>2</sub> OCH <sub>2</sub> CH=CH <sub>2</sub>	5	42	840	170

[a] General conditions: **1** = 21.05 μmol, TBAB = 8 equiv, CH<sub>2</sub>Cl<sub>2</sub> = 0.3 mL, epoxide = 5 mL. Temperature = 100 °C, P<sub>CO<sub>2</sub></sub> = 10 bar.

confirmed that methyl derivatives are more active than chloride ones (cfr entries 6 and 7 in Table 3). Finally, the performance of catalyst **1** was investigated in the reactions of CO<sub>2</sub> with terminal epoxides (Scheme 3). Results are summarized in Table 4. The reactions were carried out at 100 °C and 10 bar of CO<sub>2</sub> pressure. In all cases cyclic carbonates (CCs) were obtained as exclusive product.

Cyclic carbonates from monosubstituted epoxides bearing various substituents, including halogen, aryl, alkenyl, ether and hydroxyl groups, were obtained, revealing a good tolerance of complex **1** toward different functional groups.

### NMR mechanistic studies of the CO<sub>2</sub>/CHO reaction promoted by complex **1**.

The mechanism usually proposed for the formation of cyclic carbonates involves the coordination of the epoxide to the metal centre through the oxygen atom, the following opening of the epoxide by a nucleophilic attack, the insertion of CO<sub>2</sub> into the metal-oxygen bond and finally the ring closing by an intramolecular nucleophilic attack with the formation of the cyclic carbonate.

However, in most of the papers such mechanism is proposed on the basis of theoretical studies and/or experimental results (such as kinetics analysis, stereochemistry of the products, etc), to the best of our knowledge, only in few cases intermediate species of the catalytic cycle have been observed.<sup>[15]</sup> With the aim to get a more in depth study of the mechanism active with our catalysts,

NMR studies have been carried out on reaction mixtures purposely prepared.

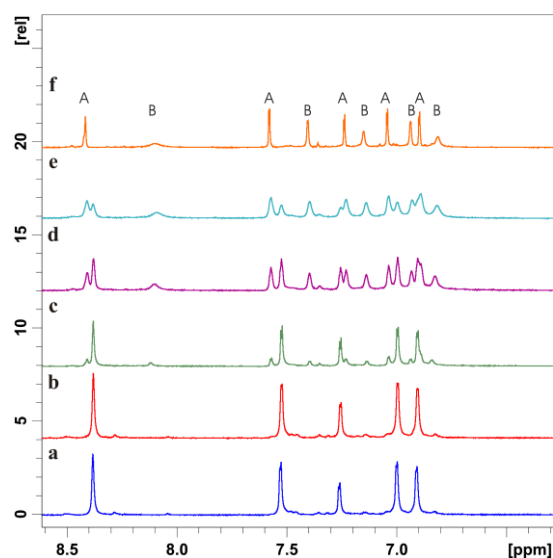
Complex **1** was first mixed with CHO and <sup>1</sup>H NMR spectroscopy was utilized to probe if the ring opening of CHO by the aluminum complex could take place. <sup>1</sup>H NMR spectra were performed with complex **1** (10 mg) and CHO (1.5 equiv) in CD<sub>2</sub>Cl<sub>2</sub> at room temperature and the formation of PCHO together with the disappearance of the CHO signals were observed in the collected spectra, in addition the signals of the starting complex remain unaltered. This suggests that complex **1** homopolymerizes the CHO in these conditions, moreover the propagation rate should be much faster than the initiation rate, so that the polymerization process involves a small percentage of the metal sites.

The same experiment was then carried out by adding one equivalent of an onium salt to the reaction mixture. In the presence of TBAC the homopolymerization process does not take place as demonstrate by the presence of the unaffected signals of the initial species, thus indicating the inhibitory effect of an additional nucleophilic species on the CHO homopolymerization.<sup>[2c]</sup> However, the subsequent addition of CO<sub>2</sub> (by gurgling the gas at one atmosphere in the CD<sub>2</sub>Cl<sub>2</sub> solution) showed the formation of new peaks in the <sup>1</sup>H NMR spectrum. The formation of the new species was followed by NMR spectra (see Figure S13 in the Supporting Information). Ten new peaks with equal intensity appeared in the aromatic region close to the initial five peaks of the starting complex (see Figure 2), indicating either the formation of a bimetallic intermediate (involving two ligands in different surroundings) or the formation of equimolar amount of two different species (A and B). Interestingly, it was observed that the reaction did not evolve towards the products if fresh CO<sub>2</sub> was not bubbled into the solution occasionally. In 8 days (and after several adding of CO<sub>2</sub>) the reaction resulted complete since the signals of the starting complex disappeared.

DOSY NMR experiment was carried out to get more insight on the products of this reaction. This experiment, indeed, providing diffusion coefficients of molecules related to hydrodynamic radius and molecular weight, may give information on the number of generated species. In our case, the aromatic region of the DOSY spectrum (Figure S14 in the Supporting Information) showed the presence of two sets of peaks lying at different diffusion coefficients, and therefore belonging to different species.

Subsequent experiments showed that the ratio between A and B could be changed by varying the reaction conditions, i.e. the reaction temperature and the amount of CHO. In details, stirring the solution at 40 °C (or even at 60 °C) and in the presence of 10 equivalents of CHO, the exclusive formation of species A was accomplished.

A full characterization of species A was carried out by means of <sup>1</sup>H, <sup>13</sup>C, HSQC and NOESY NMR spectroscopy (see Figure 3 and Figures S19-S21 in the Supporting Information). In particular, the <sup>13</sup>C NMR gave interesting information. Indeed five signals attributable to an opened epoxide were detected at 74.58 and 70.57 ppm, compatible with the CH carbons, and 37.79, 36.11 and 26.27 ppm associable to the methylene carbons (see Figure S19 in the Supporting Information).



**Figure 2.**  $^1\text{H}$  NMR aromatic region of the spectra of the reaction mixture constituted by: a) complex **1** + TBACl; b) after the addition of CHO; c) after the addition of  $\text{CO}_2$ ; d) after 2 days; e) after 4 days; f) after 8 days.

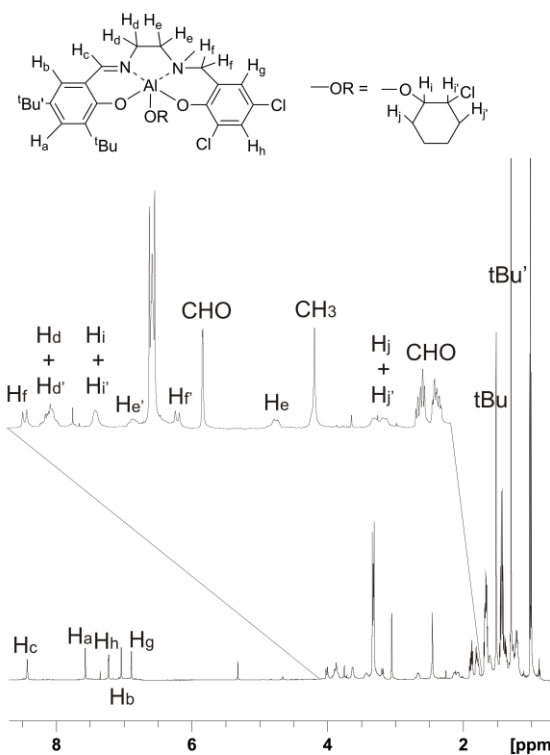
The missing signal for one of the methylene carbons may be reasonably overlapped with other signals in this area of the spectrum. The HSQC spectrum allowed us to individuate some of the corresponding signals in the  $^1\text{H}$  NMR spectrum (Figure S20). The described results allowed us to formulate the hypothesis that species A consists of the salalen ligand wrapped around an aluminum centre which also bound an opened CHO molecule. Moreover, 2D COSY and NOESY NMR spectra allowed us to attribute each signal of the  $^1\text{H}$  NMR spectrum to the different protons of the ligand skeleton in the structure of species A (see the structure depicted in Figure 3).

Even more interestingly, bubbling  $\text{CO}_2$  in the solution containing species A, and following the evolution of the reaction by means of  $^1\text{H}$  NMR, an increasing amount of CHC was observed (see S22 in the Supporting Information).

This result strongly suggests that species A is an intermediate in the catalytic cycle. In order to finally confirm this speculation, a control experiment was carried out. We first prepared this species in the NMR tube and then we used this solution in the autoclave reactor working at  $80^\circ\text{C}$  and 30 bar and in the presence of 8 equivalents of cocatalyst (see entry 1 in Table S1). Then we performed the same reaction in the presence of complex **1** and TBAC (see entry 2 in Table S1) working under the same conditions used for the reaction carried out in the presence of species A. We were delighted to observe the same conversion of CHO in the *cis*-CHC product in both cases.

Less information were gained regarding species B. As a fact, signals attributable to this species resulted broad, especially in the aliphatic region (see for example, broad signals at 3.75 and 2.17 ppm in the  $^1\text{H}$  NMR spectrum, related to signals at 59.9,

**Figure 3.**  $^1\text{H}$  NMR spectrum and hypothesized structure of species A.

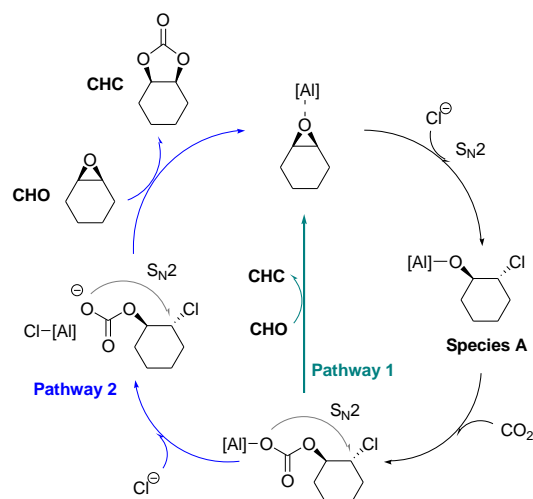


51.5 and 45.0 ppm in the  $^{13}\text{C}$  NMR spectrum, by means of HSQC spectrum, Figure S15-S17 in the Supporting Information). This made difficult the identification of all signals belonging to species B and hence the hypothesis of a plausible structure for this species. On the other hand, since species B was not observed in the reaction mixtures at temperatures higher than RT and in the presence of an excess of CHO (both conditions occurred in the autoclave reactor) we may hypothesize that species B is not involved in the catalytic cycle.

On the basis of the described results, we propose the mechanism detailed in Figure 4. Species A is the intermediate in this catalytic cycle which is formed by the  $\text{S}_{\text{N}}2$  attack of the chloride to the cyclohexene oxide coordinated to the aluminum. After the insertion of the  $\text{CO}_2$  in the Al-O bond of the species A, the reaction goes on by the  $\text{S}_{\text{N}}2$  attack of the oxygen of the carbonate group to the carbon bearing the chloride, thus furnishing the *cis*-cyclohexene carbonate and the free chloride. Reasonably, in the presence of one equivalent of cocatalyst (such as in the NMR tube experiments) the reaction follows pathway 1, whereas in the autoclave reactor, where an excess of cocatalyst is present, the ring closing reaction may take place after the displacement of the carbonate ion promoted by the excess of chloride (pathway 2). In both cases the double  $\text{S}_{\text{N}}2$  attack preserves the original configuration of the cyclohexene oxide allowing the formation of *cis*-cyclohexene carbonate.<sup>[4b,16]</sup>

**Figure 4.** Proposed mechanism for the formation of *cis*-cyclohexene carbonate promoted by complex **1**/TBAC.

## Conclusions



The fixation of CO<sub>2</sub> in cyclic carbonate products was realized by its reaction with some epoxides, catalyzed by salalen aluminum complexes. The reaction conditions were varied in the cyclohexene oxide/CO<sub>2</sub> cycloaddition reaction in order to maximize the production of *cis*-cyclohexene carbonate. *Cis*-CHC was obtained as exclusive product with good TON values (from 106 to 1290) even operating at 2 bar of CO<sub>2</sub>, in the presence of an ammonium salt as cocatalyst. Changing the substituents on the ligand skeleton showed that electron withdrawing substituents have a beneficial effect on the activity of the catalyst. The comparison of salen, salan and salalen aluminum complexes bearing the same substitution pattern on the different ligands indicated that the salen aluminum complex was the most active in the CHO/CO<sub>2</sub> reaction. The scope of the reaction was investigated by exploring the reaction of CO<sub>2</sub> with different terminal epoxides showing a good tolerance of complex **1** toward different functional groups. NMR analysis of reaction mixtures allowed to shed light on the reaction mechanism. Interestingly, an intermediate species of the catalytic cycle was individuated and characterized by NMR spectroscopy. A control experiment showed that this species was catalytically active, allowing us to propose a catalytic cycle for the formation of *cis*-cyclohexene carbonate promoted by these salalen aluminum complexes.

## Experimental Section

Further experimental details and characterization data are included in the Supporting Information. CCDC 1507131 contains the supplementary crystallographic data for this paper in CIF format. These data are provided free of charge by the Cambridge Crystallographic Data Center.

### Materials

All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk-line techniques under a dry nitrogen atmosphere or using a Braun Labmaster glove box. All solvents and reagents were obtained from commercial sources (Aldrich and Merck). The aluminum precursors, AlMe<sub>3</sub> and AlEt<sub>2</sub>Cl, were purchased from Aldrich and used as received. Benzene, hexane and toluene were distilled over sodium benzophenone. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and

*This is the pre-peer reviewed version of the following article: ChemSusChem 2017, 10, 1217 – 1223, which has been published in final form at DOI : 10.1002/cssc.201601479. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.*

dried over activated 3-Å molecular sieves prior to use. Propylene oxide, (±)-epichlorohydrin, glycidol, allyl glycidyl ether, styrene oxide and cyclohexene oxide were distilled under reduced pressure over calcium hydride and stored in a sealed flask in a glove box. Glassware and autoclave used in the polymerization were dried in an oven at 120 °C overnight and exposed to vacuum-nitrogen cycles thrice.

### Synthesis of Salalen Ligands

The ligands were prepared according to published procedures<sup>[8,17]</sup> which involves the reaction of condensation of *N*-methyl-1,2-diaminoethane with a substituted salicylaldehyde followed by nucleophilic substitution on a substituted bromomethylphenol. The identity of the compounds was determined by <sup>1</sup>H NMR.

### Synthesis of Aluminum Complexes

A representative procedure for the preparation of complex **1** is given, see Supporting Information for further details for all other complexes. H<sub>2</sub>L<sub>1</sub> (0.200 g, 4.30 · 10<sup>-4</sup> mol) was dissolved in dry benzene (2 mL) to which AlMe<sub>3</sub> (97% wt, 0.0319 g, 4.30 · 10<sup>-4</sup> mol) was added and stirred at room temperature for 2 hours. Afterwards the solvent was removed in vacuo and the solid residue was washed with pentane. Complex **1** was obtained as a yellow powder.

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ -0.42 (s, 3H, Al-CH<sub>3</sub>), 1.37 (s, 9H, CCH<sub>3</sub>), 1.58 (s, 3H, N-CH<sub>3</sub>), 1.81 (s, 9H, CCH<sub>3</sub>), 2.01 (m, 1H, CH<sub>2</sub>), 2.35 (d, *J* = 12.80 Hz, 1H, CH<sub>2</sub>), 2.53 (m, 1H, CH<sub>2</sub>), 3.13 (d, *J* = 12.80 Hz, 1H, CH<sub>2</sub>), 6.67 (d, *J* = 2.40 Hz, 1H, Ar-H), 6.77 (d, *J* = 2.40 Hz, 1H, Ar-H), 7.27 (s, 1H, C=N), 7.43 (d, *J* = 2.65 Hz, 1H, Ar-H), 7.74 (d, *J* = 2.56 Hz, 1H, Ar-H).

<sup>13</sup>C NMR (250 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ -9.15 (AlCH<sub>3</sub>), 29.90 (CCH<sub>3</sub>)<sub>3</sub>, 31.62 (CCH<sub>3</sub>)<sub>3</sub>, 34.19 (CCH<sub>3</sub>)<sub>3</sub>, 35.74 (CCH<sub>3</sub>)<sub>3</sub>, 43.91 (N-CH<sub>3</sub>), 50.96 (CH<sub>2</sub>), 54.29 (CH<sub>2</sub>), 57.80 (CH<sub>2</sub>), 117.58 (Cq), 120.59 (Cq), 125.32 (Cq), 125.73 (Cq), 127.43 (CH), 129.81 (CH), 132.15 (CH), 137.47 (Cq), 141.61 (Cq), 155.33 (Cq), 165.59 (Cq), 173.52 (CH=N).

### CO<sub>2</sub>/Epoxide Reaction Procedure

In a typical experiment, in a glove box, catalyst and cocatalyst (TBAX, X=Br, Cl, OAc; PPNCl) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.3 mL) and then the epoxide (5 mL) was added. The reaction was carried out in an autoclave pressurized to the appropriate pressure of CO<sub>2</sub>, whilst the reaction mixture was stirred for 20 minutes at room temperature, in order to facilitate CO<sub>2</sub> dissolution. Then the reaction mixture was stirred at the desired temperature. After the prescribed time, the reaction mixture was quenched by dipping the autoclave in an ice bath, and adding 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub> at air. The conversion of epoxide to cyclic carbonate was determined by analysis of the sample by <sup>1</sup>H NMR spectroscopy.

## Acknowledgements

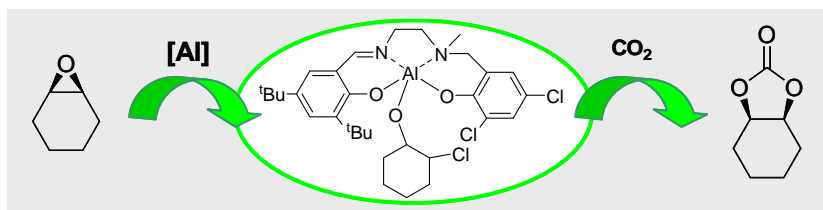
The authors thank Dr. Patrizia Iannece for elemental analysis and Dr. Patrizia Oliva for NMR technical assistance. This work was supported by the Italian Ministry of University and Research (PRIN 2010–2011: nanostructured polymeric materials with tailored molecular and crystalline structures, for advanced technologies and for the environment).

**Keywords:** Carbon dioxide capture • cycloaddition • homogeneous catalysis • N,O ligands • reaction mechanism

- [1] a) M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T. E. Müller, *ChemSusChem* **2011**, *4*, 1216–1240; b) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem.* **2011**, *123*, 8662–8690; *Angew. Chem., Int. Ed.* **2011**, *50*, 8510–8537; c) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709–1742; d) M. Poliakkoff, W. Leitner, E. S. Streng, *Faraday Discuss.* **2015**, *183*, 9–17.
- [2] a) G. W. Coates, D. R. Moore, *Angew. Chem.* **2004**, *116*, 6784–6804; *Angew. Chem., Int. Ed.* **2004**, *43*, 6618–6639; b) M. R. Kember, A. Buchard, C. K. Williams, *Chem. Commun.* **2011**, *47*, 141–163; c) M. Taherimehr, P. P. Pescarmona, *J. Appl. Polym. Sci.* **2014**, *121*, 41141–41158.
- [3] M. North, R. Pasquale, C. Young, *Green Chem.* **2010**, *12*, 1514–1539.
- [4] a) J. W. Comerford, I. D. V. Ingram, M. North, X. Wu, *Green Chem.* **2015**, *17*, 1966–1987; b) C. Martin, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, *5*, 1353–1370.
- [5] a) J. Meléndez, M. North, R. Pasquale, *Eur. J. Inorg. Chem.*, **2007**, 3323–3326; b) M. North, R. Pasquale, *Angew. Chem.* **2009**, *121*, 2990–2992; *Angew. Chem., Int. Ed.* **2009**, *48*, 2946–2948; c) W. Clegg, R. Harrington, M. North, R. Pasquale, *Chem.–Eur. J.* **2010**, *16*, 6828–6843; d) C. Beattie, M. North, P. Villuendas, C. Young, *J. Org. Chem.* **2013**, *78*, 419–426; e) J. Meléndez, M. North, P. Villuendas, *Chem. Commun.* **2009**, 2577–2579; f) J. Meléndez, M. North, P. Villuendas, C. Young, *Dalton Trans.* **2011**, *40*, 3885–3902.
- [6] a) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, *J. Am. Chem. Soc.* **2013**, *135*, 1228–1231; b) C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo, A. W. Kleij, *Chem. - Eur. J.* **2014**, *20*, 2264–2275; c) J. Rintjema, W. Guo, E. Martin, E. C. Escudero-Adán, A. W. Kleij, *Chem. - Eur. J.* **2015**, *21*, 10754–10762; d) J. Rintjema, R. Epping, G. Fiorani, E. Martin, E. C. Escudero-Adán, A. W. Kleij, *Angew. Chem.* **2016**, *128*, 4040–4044; *Angew. Chem., Int. Ed.* **2016**, *55*, 3972–3976.
- [7] M. Cozzolino, K. Press, M. Mazzeo, M. Lamberti, *ChemCatChem* **2016**, *8*, 455–460.
- [8] a) A. Pilone, N. De Maio, K. Press, V. Venditto, D. Pappalardo, M. Mazzeo, C. Pellecchia, M. Kol, M. Lamberti, *Dalton Trans.* **2015**, *44*, 2157–2165; b) E. L. Whitelaw, G. Loraine, M. F. Mahon, M. D. Jones, *Dalton Trans.* **2011**, *40*, 11469–11473
- [9] D. J. Darensbourg, D. R. Billodeaux, *Inorg. Chem.* **2005**, *44*, 1433 – 1442
- [10] H. Sugimoto, H. Ohtsuka, S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4172–4186.
- [11] P. Hornnirun, E. L. Marshall, V. C. Gibson, R. I. Pugh, A. J. P. White, *PNAS* **2006**, *103*, 15343–15348.
- [12] P. Hornnirun, E. L. Marshall, V. C. Gibson, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2004**, *126*, 2688–2689.
- [13] a) N. Ikpo, J. C. Flogeras, F. M. Kerton, *Dalton Trans.* **2013**, *42*, 8998–9006; b) A. Decortes, A. M. Castilla, A. W. Kleij, *Angew. Chem.* **2010**, *17*, 10016–10032; *Angew. Chem. Int. Ed.* **2010**, *49*, 9822–9837.
- [14] D. Rutherford, D. A. Atwood, *Organometallics* **1996**, *15*, 4417–4422.
- [15] a) J. A. Castro-Osma, M. North, W. K. Offermans, W. Leitner, T. E. Muller, *ChemSusChem* **2016**, *9*, 791–794; b) D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2003**, *125*, 11911–11924.
- [16] G. A. Luinstra, G. R. Haas, F. Molnar, V. Bernhart, R. Eberhardt, B. Rieger, *Chem. Eur. J.* **2005**, *11*, 6298–6314.
- [17] a) A. Yeori, S. Gendler, S. Groysman, I. Goldberg, M. Kol, *Inorg. Chem. Commun.*, **2004**, *7*, 280–282; b) K. Press, A. Cohen, I. Goldberg, V. Venditto, M. Mazzeo, M. Kol, *Angew. Chem.* **2011**, *123*, 3591–3594; *Angew. Chem. Int. Ed.* **2011**, *50*, 3529–3532; c) K. Press, V. Venditto, I. Goldberg, M. Kol, *Dalton Trans.* **2013**, *42*, 9096–9103.

Entry for the Table of Contents

FULL PAPER



One intermediate species in the cycloaddition reaction of CO<sub>2</sub> and cyclohexene oxide, promoted by salalen aluminum complexes, was individuate and characterized by NMR spectroscopy.

Mariachiara Cozzolino, Tomer Rosen,  
Israel Goldberg, Mina Mazzeo and  
Marina Lamberti\*

Page No. – Page No.

**Selective Synthesis of Cyclic  
Carbonate by Salalen Aluminum  
Complexes and Mechanistic Studies**