

SALEN ALUMINIUM COMPLEX AND ITS USE AS A CATALYST

The invention is directed to an optionally substituted salen aluminium complex and the use of this complex as part of a catalyst for reactions involving an epoxide compound and carbon dioxide.

Substituted salen aluminium complexes are known components of catalyst systems for converting an epoxide compound with carbon dioxide. Such a reaction can be directed to the production of a cyclic carbonate compound or can be a copolymerisation process to prepare aliphatic polycarbonates or polyesters.

WO2010/106324 describes a process to prepare cyclic carbonate compounds from carbon dioxide and an epoxide compound using a catalyst system comprising of an oxo-dimer of a substituted salen aluminium complex. The two nitrogen atoms of the salen structure are connected via a bridging group. Disclosed bridging groups are phenylene, C5-heterocycle and ethylene. In the presence of tetra butyl ammonium bromide (TBAB) acting as a co-catalyst these dimeric aluminium(salen) complexes are highly active homogeneous catalysts for the reaction of epoxides with carbon dioxide to produce cyclic carbonates. The reaction can be carried out at room temperature and atmospheric pressure, using short reaction times and commercially viable amounts of catalyst.

WO2009109765 describes dimeric aluminium(salen) complexes similar to those described in WO2010/106324 which are immobilized on a solid support via an anchoring group which consists of a quaternary ammonium ion paired with a bromide ion. The anchoring group acts as the earlier referred to co-catalyst. This heterogeneous catalyst is also found to be highly active catalysts for the reaction of epoxides with carbon dioxide to produce cyclic carbonates at moderate temperatures and atmospheric pressures.

EP3728213B1 describes a process to prepare cyclic carbonate compounds from carbon dioxide and an epoxide compound in a suspension of a heterogeneous catalyst. The heterogeneous catalyst is a supported oxo-dimer of a substituted salen aluminium ligand as for example described in
5 WO2009109765. Benzyl bromide is present in the solution for maintaining catalyst activity.

An advantage of the catalyst as described in WO2009109765 and EP3728213B1 is that the catalysed process for preparing a cyclic carbonate
10 compound from carbon dioxide and an epoxide compound can be performed at moderate temperatures and pressures. A problem is that the supported salen aluminium ligand is difficult to prepare requiring at least 9 synthesis steps. Some of these steps have a low yield resulting in an overall yield of less than 10% and large amounts of solvents are used in the synthesis process.

15 In ANTONELLO DECORTES ET AL: "Ambient Fixation of Carbon Dioxide using a Zn(II) salphen Catalyst", CHEMCATCHEM, JOHN WILEY & SONS, INC; HOBOKEN, USA, part 3, nr. 5, 2 March 2011 (2011-03-02), pages 831-834, XP072430479, ISSN: 1867-3880, DOI: 10.1002/CCTC.201100031 describes a Zn(II) salphen used as part of a catalyst in a process to prepare a cyclic carbonate compound from epoxyhexane and carbon dioxide at 1 MPa CO₂ pressure in an inert reaction solvent, ie dichloromethane (DCM). The catalytic activity of complexes with different metals are compared. The bridging group connecting the nitrogen atoms in these complexes, the 'en' bridge, is
20 phenylene. The catalytic activity of zinc complexes having other bridging groups are compared in this publication at 1 MPa CO₂ pressure. The complex with a methyl alkylated pyridinium bridging group did not show any catalytic activity.

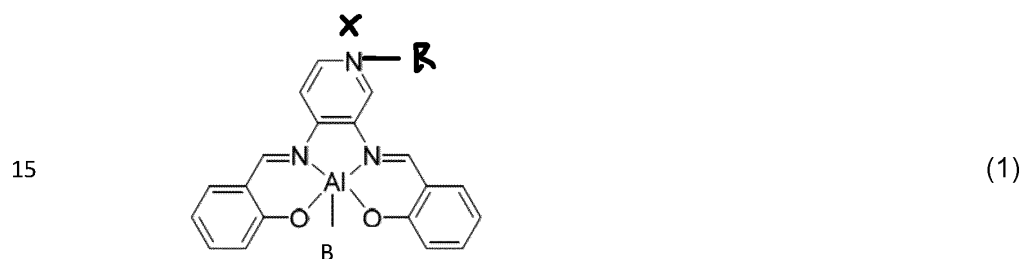
30 MARTIN C. ET AL: "Easily accessible bifunctional Zn(salpyr) catalysts for the formation of organic carbonates", CATALYSIS SCIENCE & TECHNOLOGY, part 4, nr. 6, 23 January 2014 (2014-01-23), pages 1615-1621, XP093114624, ISSN: 2044-4753, DOI: 10.1039/C3CY01043K describes

a bifunctional Zn(salpyr) complex having methyl alkylated pyridinium bridging group. The complex is used as part of a catalyst system to prepare a cyclic carbonate compound from epoxyhexane and carbon dioxide at a CO₂ pressure of 1 MPa. The experiments were executed in pure epoxyhexane.

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The aim of the present invention is to provide a complex which can be used as part of a catalyst in the preparation of a cyclic carbonate from an epoxide and carbon dioxide at low pressure.

- 10 This is achieved by the following optionally substituted salen aluminium complex having the following general formula (1)



- 20 wherein B is a halogen, alkoxy or alkyl group, and wherein the phenyl groups of the salen aluminium complex are optionally substituted, where R is a hydrocarbon group and X is a halogen anion.

- 25 Applicants found that this novel complex is catalytically active at the desired lower pressures. Further the salen aluminium complex can be prepared in a more simple manner, requiring less synthesis steps and in a substantially higher yield, than the prior art oxo-dimer of a substituted salen aluminium ligand. It has been found that the aluminium complex having a pyridine bridge can be alkylated with different alkyl bromides enabling functionalisation and immobilisation of the complex. The quaternary nitrogen ion of the pyridinium bridging group acts as a co-catalyst of the catalyst system. The optionally substituted complex having a pyridine bridging group is a novel intermediate product when preparing a corresponding optionally substituted complex having the pyridinium bridging group. The optionally substituted complex having a pyridine bridging group may also be used as part of a homogeneous or
- 30

heterogeneous catalyst for the reaction of epoxides with carbon dioxide to produce cyclic carbonates.

5 The invention is also directed to the following process for preparing the optionally substituted salen aluminium complex having a pyridinium bridging group.

Process to prepare an optionally substituted salen aluminium complex having a pyridinium bridging group starting from a corresponding optionally substituted salen nickel or zinc complex having a pyridine bridging group,
10 wherein the following steps are performed:

(a) demetallizing the corresponding optionally substituted salen nickel or zinc complex to obtain a demetallized salen ligand, and

(b) contacting the demetallized salen ligand of step (a) with an aluminium compound to obtain the optionally substituted salen aluminium intermediate complex having a 3-pyridine bridge and
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(c) subjecting the optionally substituted salen aluminium intermediate complex having a 3-pyridine bridge to an alkylation to obtain the corresponding optionally substituted salen aluminium complex having a 3-pyridinium bridging group.
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Further advantages will be discussed when describing the invention in more detail.

25 The pyridine bridging group is a 3-pyridine group bridging group. The pyridine bridging group is a 3-pyridine group.

The alkoxy group B in formula (1) may be a methoxy, ethoxy and/or isopropoxy group. The alkyl group B may have 1-5 carbon atoms, such as for example methyl or ethyl. B may also be chloride, bromide or iodide. The choice
30 of B may depend on the availability of the starting aluminium compound when synthesizing the complex. For this reason B is preferably chloride.

The anion X in formula (1) is suitably a halogen anion, preferably a iodide anion or a bromide anion and even more preferably a bromide anion. The complexes based on iodide or preferably bromide are preferred when used as part of a catalyst system. The halogen anion X of choice will be referred to as the catalyst system halogen.

The phenyl groups in formula (1) are suitably substituted at their 3 - position. The phenyl groups in formula (1) may be substituted with halogen, optionally substituted C1-20 alkyl, optionally substituted C5-20 aryl, optionally substituted C3-20 heterocyclyl, ether, ammonium and nitro groups. Preferably they are substituted at their 3-position, optionally also at their 5-position. Examples are described in EP2146977. Preferably the phenyl groups are substituted with a butyl group and more preferably with a tert.-butyl group at their 3-position and optionally also at their 5-position.

Group R in formula (1) may be any group such as optionally substituted C1-20 alkyl, optionally substituted C5-20 aryl, optionally substituted C3-20 heterocyclyl groups. Examples of possible groups are benzyl and C3-C10 alkyl groups, for example propyl, butyl, pentyl, hexyl, heptyl, octyl and nonyl.

Preferably R in formula (1) is an anchor group to immobilize the salen aluminium complex to a carrier to obtain a supported catalyst. R may thus be an anchoring group to covalently anchor the optionally substituted salen aluminium ligand to a heterogeneous support as the carrier. The suitable anchor group is a group which can bind the ligand to the heterogeneous support and will depend on the type of heterogeneous support. When the support has silanol groups (Si-OH) such as for a silica support or aluminol groups (Al-OH) such as for an alumina support, the anchoring group is preferably an alkyl(trialkoxo)silane or alkyltrichlorosilane which can form a covalent bond with the silanol groups. Examples of suitable alkyl(trialkoxo)silane or alkyltrichlorosilane groups are propyl(trimethoxy)silane, propyl(triethoxy)silane, propyltrichlorosilane, propyl(alkyl)dichlorosilane and propyl(dialkyl)chlorosilane. Other possible anchoring groups are styryl(trialkyl)silane, propylbis(methylallyl)silane, propyl tris(methylallyl)silane,

propylphosphoric acid, propyl(dialkyl)phosphonate, and alkyl-1,1 bisphosphonic acid.

The heterogeneous support may be relatively large particles which may be present in a reactor as a packed bed. The supported catalyst may also be used as a suspension in the reaction mixture. The heterogeneous support will then be present as a powder having dimensions which are small enough to create a high active catalytic surface per weight of the heterogeneous support and large enough to be easily separated from the cyclic carbonate in or external of the reactor. Preferably the heterogeneous support powder particles have for at least 90 wt% of the total particles a particle size of above 10 μm and below 2000 μm . The particle size is measured by a Malvern® Mastersizer® 2000.

The invention is also directed to especially the following specific complexes:

[Al(3,4-Py-Salphen(N-Propyl(trimethoxy)silane))(Cl)]Br,
[Al(3,4-Py-Salphen(N-Propyl(triethoxy)silane))(Cl)]Br ,
[Al(3,4-Py-Salphen(N-Propyl(triethoxy)silane))(OEt)]Br ,
[Al(3,4-Py-Salphen(N-Propyl(triethoxy)silane))(Cl)]I,
[Al(3,4-Py-Salphen(N-Propyl(diethoxyphosphonate)(Cl)]Br ,
[Al(3,4-Py-Salphen(N-Propyl(phosphoric acid)(Cl)]Br ,
[Al(3,4-Py-Salphen(N-Butyl(diethyl phosphonate)(OEt)]Br , and
[Al(3,4-Py-Salphen(N-Pentyl(phosphoric acid)(Cl)]Br,

wherein for the above complexes optionally a substituent group is present at the 3-position of the phenyl groups of the salphen structure and preferably a tert-butyl group at the 3-position and optionally also at the 5-position. Et is ethyl in the above descriptions.

Examples of demetallized salen ligands which after metalation result in a complex according the invention are illustrated in Figure 1.

The invention is also directed to a supported aluminium complex comprising the complex according to the invention and a heterogeneous

support. The support is preferably a silica, alumina or silica-alumina support. The complex may be immobilized via a substituent on the phenyl group, such as for example a diethylaminomethyl group as for example described in EP2257559. Preferably the complex is immobilized on the surface of the support by means of group R of formula (1) serving as an anchoring group.

The starting optionally substituted salen nickel or zinc complex having a pyridine bridging group may be obtained by well known synthesis routes such as for example described in Catal. Sci. Technol., 2014, 4, 1615, ChemCatChem 2011, 3, 831 – 834.

In step (a) the corresponding optionally substituted salen nickel or zinc complex is demetallized to obtain a demetallized salen ligand. Demetallation may be performed by known demetallation processes such as for example described in Organometallics 2002, 21, 14, 2950–2957. The demetallation is suitably performed in a water-free demetallation process in the presence of imidazole in acetonitrile or in toluene, preferably toluene. This step is performed in a high yield.

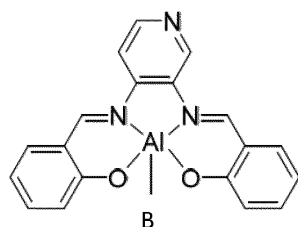
In Step (b) the demetallized salen ligand of step (a) is contacted with an aluminium compound. This aluminium compound comprises a precursor for group B as used in this description to illustrate the preferred complexes. When B is chloride the aluminium compound is suitably diethylaluminium chloride ($\text{Al}(\text{Et})_2\text{Cl}$). When B is an alkoxy group, such as ethoxy the aluminium compound is preferably triethoxide aluminium. When B is an alkyl group the aluminium compound is suitably a trialkyl aluminium compound, preferably wherein the alkyl group has 1-5 carbon atoms, such as for example trimethyl aluminium and triethyl aluminium.

Preferably the aluminium compound is added gradually in step (b) to the demetallized salen ligand as dissolved or dispersed as a slurry in a suitable solvent when the process is performed at a larger scale to enhance the contacting of the reagents. It is found that if the aluminium compound is not

added gradually the reaction mass solidifies and effective mixing of the reagents is not possible. The demetallized salen ligand is preferably dissolved or dispersed as a slurry in a suitable solvent, like for example toluene or THF (tetrahydrofuran). The gradual addition is preferably performed for more than 1
5 hours and preferably more than 1.5 hours. Preferably the addition continues for not more than 3 hours. The temperature is preferably between 20 and 90 °C, more preferably between 50 and 80 °C. Preferably a C5-C10 hydrocarbon alkane solvent, preferably heptane, is added to lower the solubility of the obtained optionally substituted salen aluminium complex. The solidified
10 complex may be separated from the solvents by filtration.

The corresponding optionally substituted salen aluminium complex having a pyridinium bridging group as in formula (1) is prepared in a step (c). In step (c) the optionally substituted salen aluminium complex having a pyridine
15 bridge as obtained in step (b) is subjected to an alkylation reaction to obtain the corresponding optionally substituted salen aluminium complex having a pyridinium bridging group. The alkylation is suitably performed by contacting the optionally substituted salen aluminium complex having a pyridine bridge in a suitable solvent with a halogen-R compound. The halogen may be the system
20 halogen or a different halogen. Preferably the halogen-R is a bromide compound, Br-R, where R is as described above. A suitable solvent is tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) or mixtures of dimethyl sulfoxide (DMSO) and acetonitrile. It has been found advantageous to perform the alkylation starting with the optionally substituted
25 salen aluminium complex instead of alkylating the starting optionally substituted salen zinc complex having a pyridine bridging group. It has been found not possible to subject the zinc complex to the alkylation with a bromide compound, Br-R. Starting with the aluminium complex such an alkylation with Br-R is possible enabling the preparation of the complex of this invention wherein X is
30 a bromide ion. When preparing the complex having the pyridinium bridging group the complex having the pyridine bridging group may be regarded as a novel and inventive intermediate compound.

The invention is thus also directed to an optionally substituted salen aluminium intermediate complex:



10 wherein B is a halogen, alkoxy or alkyl group and wherein the phenyl groups of the salen aluminium complex are optionally substituted as described above.

15 The invention is also directed to a process to prepare an optionally substituted salen aluminium intermediate complex as described above starting from a corresponding optionally substituted salen nickel or zinc complex having a pyridine bridging group, wherein the following steps are performed:

(a) demetallizing the corresponding optionally substituted salen nickel or zinc complex to obtain a demetallized salen ligand, and

20 (b) contacting the demetallized salen ligand of step (a) with an aluminium compound to obtain the optionally substituted salen aluminium intermediate complex. Steps (a) and (b) are suitably performed as earlier described.

25 The invention is also directed to a process to prepare an optionally substituted salen aluminium intermediate complex according to this invention from an optionally substituted salen aluminium intermediate complex according to this invention, wherein the optionally substituted salen aluminium intermediate complex is subjected to an alkylation as described above to obtain the optionally substituted salen aluminium intermediate complex.

30 The invention is also directed to a catalyst system comprising a complex according to this invention or a supported aluminium complex according to this invention and a co-catalyst. This co-catalyst may be every compound which provides a bromide anion or an iodide anion as the catalyst system halogen.

This compound may be organic or inorganic. The optionally substituted salen complex may advantageously be used as a catalyst system. Because the complex has a pyridinium halogen salt the complex may be used as catalyst in the absence of an added halogen salt. Typical added halogen salts for such catalyst systems as co-catalysts are a bromide salt or an iodide salt. The bromide salt may be a quaternary ammonium bromide salt, such as for example tetrabutyl ammonium bromide (TBAB) or a phosphonium bromide salt and the iodide salt may be a quaternary ammonium iodide salt or a phosphonium iodide salt. When the complex of this invention is used the catalysed process may be performed in the absence of such an added halogen salt or in the presence of less added halogen salt.

The catalyst system may be used as a catalyst or as part of a catalyst in a copolymerisation process to prepare aliphatic polycarbonates starting from an epoxide compound and carbon dioxide. Another reaction where the catalyst system may be used is in a process to prepare a polyester by ring-opening polymerisation of a lactone compound as for example described in WO2012/065711 or by ring-opening polymerisation of a maleic anhydride

Preferably the catalyst system is used as a catalyst or as part of a catalyst in a process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide.

The invention is therefore also directed to a process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide in the presence of the catalyst system. The catalyst system preferably comprises next to the complex of this invention a separate halogen salt, such as the aforementioned a bromide salt or an iodide salt.

The molar ratio between the optionally substituted salen aluminium ligand having a pyridinium bridge and the bromide salt expressed as Al/Br (mol/mol) is preferably between 0.1 and 20, more preferably between 1 and 8 and most preferably between 2 and 5.

The starting epoxide compound suitably has 2 to 8 carbon atoms. Suitable epoxide compounds are ethylene oxide, propylene oxide, butylene oxide, pentene oxide, glycidol, styrene oxide, epichlorohydrin or fluoroethylene oxide.

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The carbon dioxide is suitably contacted with the epoxide compound in a liquid also comprising the catalyst system. The liquid may be an inert solvent. Possible inert solvents are toluene, cyclic carbonate compounds and/or preferably the cyclic carbonate product itself. The supported catalyst may also be used as a suspension in the reaction mixture. The carbon dioxide is suitably contacted with the epoxide compound in the suspension of the afore mentioned inert solvent, preferably the liquid cyclic carbonate, and the heterogeneous catalyst. The temperature and pressure conditions are chosen such that the cyclic carbonate is in its liquid state. The temperature and pressure conditions are further chosen such that carbon dioxide and epoxide easily dissolve in the liquid cyclic carbonate reaction medium. The temperature may be between 0 and 200 °C and the pressure between 0 and 5.0 MPa (absolute) and wherein temperature is below the boiling temperature of the cyclic carbonate product at the chosen pressure. At the high end of these temperature and pressure ranges complex reactor vessels will be required. Because favourable results with respect to selectivity and yield to the desired carbonate product are achievable at lower temperatures and pressures it is preferred that the temperature is between 20 and 150 °C, more preferably between 40 and 120 °C, and the absolute pressure is between 0.1 and 0.5 MPa, more preferably between 0.1 and 0.3 MPa. The partial pressure of carbon dioxide will be lower or equal to this pressure.

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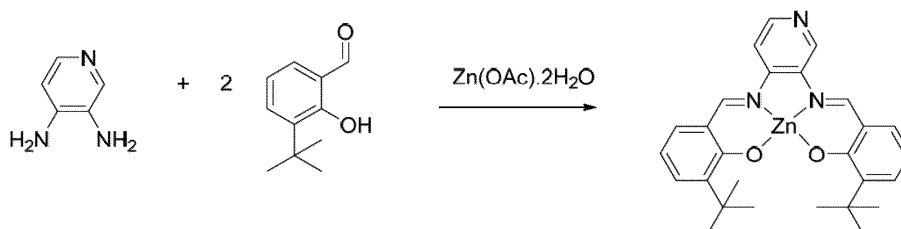
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Example 1

In this example a [Zn(3,4-Py Salphen)] according to the below scheme is prepared.



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A round bottom flask was charged with 3,4-diamine pyridine (1.44 gr. 13.2 mmol), 3-tert butyl salicylaldehyde (4.8 mL, 28.0 mmol), zinc acetate dihydrate (3.08 g, 13.8 mmol), triethyl amine (5.0 mL, 35.9 mmol) in 100 mL methanol. The mixture was stirred and heated to reflux for 24 hours providing a bright red solid. The solid was filtered off and washed with methanol (3 x 20 mL). The yield of the [Zn(3,4-Py Salphen)] is 6.24 gram (95.6%).

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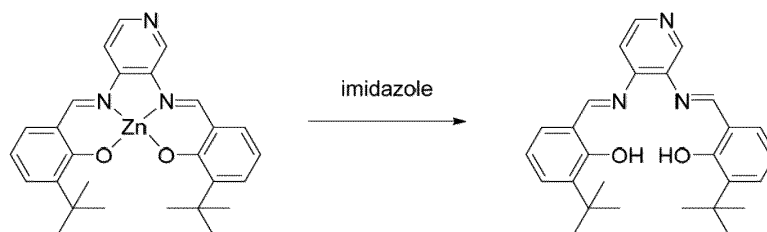
The product was characterised by ¹H-NMR: ¹H NMR (300 MHz, DMSO-d₆) δ 9.20 (s, 1H), 9.15 (s, 2H), 8.48 (d, J = 5.5 Hz, 1H), 7.88 (d, J = 5.5 Hz, 1H), 7.29 (m, 4H), 6.48 (td, J = 7.5, 3.2 Hz, 2H), 1.48 (s, 18H). The NMR data indicates that the desired product was formed.

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Example 2

In this example step (a) of the process to prepare the complex according to the invention is illustrated. The [Zn(3,4-Py Salphen)] as obtained in Example 1 is demetallized according to the below scheme.

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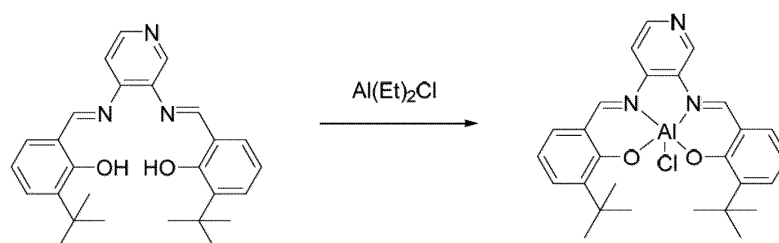


A flask was charge with the [Zn(3,4-Py-Salphen)] (6.24 gram, 12.65 mmol) of Example 1 and dissolved in 60 mL toluene. To this solution, imidazole (3.48 g, 50.6 mmol) was added heated to 60 °C for 2 hours. The solids were filtered off and washed with toluene. Alternative solvents for toluene are methanol and MTBE. The solid again taken up in methanol (60 mL) and heated 60 °C for 2 hours. The solids were filtered off and dried yielding 4.27 grams of an orange powder. Yield 78.6%.

The product was characterised by ¹H-NMR: ¹H NMR (300 MHz, DMSO-d₆) δ 13.80 (s, 1H), 13.73 (s, 1H), 9.07 (d, J = 8.7 Hz, 2H), 8.71 (s, 1H), 8.58 (d, J = 5.3 Hz, 1H), 7.62 – 7.48 (m, 3H), 7.42 (td, J = 8.0, 1.7 Hz, 2H), 6.95 (td, J = 7.7, 3.3 Hz, 2H), 1.38 (s, 18H). The NMR data indicates that the desired product was formed.

Example 3

In this example step (b) of the process to prepare the intermediate complex according to the invention is illustrated. The substituted salen aluminium complex having a pyridine bridge is prepared from the demetallized ligand obtained in Example 2 according to the below scheme.



In a flame dried Schlenk, 3,4-Py Salphen ligand (2.6 g. 6.0 mmol) as obtained in Example 2 was dissolved in 24 mL toluene and heated to 60 °C. The Al(Et)₂Cl (1.8 M in toluene, 6.4 mL. 11.6 mmol) was added and the reaction was stirred for 17 hours. The reaction was cooled down to room temperature and the product was filtered off and washed with toluene (10 mL) and pentane (2 x 10 mL) yielding a yellow solid (1.19 g. 40%).

The product was characterised by ^1H -NMR: ^1H NMR (300 MHz, DMSO-
d6) δ 9.50 (s, 1H), 9.44 (d, J = 5.0 Hz, 2H), 8.65 (d, J = 5.6 Hz, 1H), 8.13 (d, J =
5.7 Hz, 1H), 7.57 (td, J = 11.8, 10.6, 4.8 Hz, 4H), 6.90 – 6.75 (m, 2H), 1.56 (d, J
= 1.8 Hz, 19H). The NMR data indicates that the desired product was formed.

Example 3a

Example 3 was repeated except that $\text{Al}(\text{OEt})_3$ was used as the B-
containing aluminium compound and 2,3-Py-Salphen was used to obtain a 2,3-
Py-Salphen complex wherein B is ethoxy.

In a flame-dried Schlenk, 2,3-Py Salphen ligand (0.2 g) was dissolved in
dry toluene (9 ml) and heated at reflux. The aluminum triethoxide (0.151 g) was
added, followed by 2 ml toluene, and the reaction was stirred for 17 hours. The
reaction cooled down to room temperature and the product was filtered off and
washed 3 times with 5 ml toluene. The solid was dried under vacuum. Yield:
43%

The product was characterised by ^1H NMR (300 MHz, Chloroform-d) δ
9.80 (s, 1H), 8.94 (s, 1H), 8.51 – 8.37 (d, J =4.1 Hz, 1H), 8.04 (d, J = 8.1 Hz,
1H), 7.61 (t, J = 8.6 Hz, 2H), 7.47 (d, J = 7.4, 1H), 7.38 – 7.25 (m, 2H), 6.85 (q,
 J = 8.1 Hz, 2H), 3.41 (q, J = 6.9 Hz, 2H), 1.64 (s, 18H), 0.76 (t, J = 6.9 Hz, 3H).
The NMR data indicates that the desired product was formed.

Example 3b

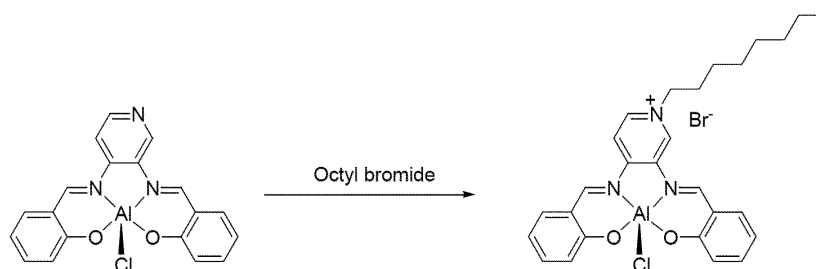
Example 3 is repeated at a larger scale wherein 3,4-Py Salphen ligand
(327.32 g, 0.76 mol) is loaded in a dried 5L reactor under nitrogen stream
followed by adding 1 L toluene and 0.5 L heptane. The reaction mixture is
stirred by overhead stirrer and warmed up to 60°C. When the 3,4-Py Salphen
ligand is dissolved the $\text{Al}(\text{Et})_2\text{Cl}$ (1.0M in hexane, 800 mL, 0.8 mol) is added
over the course of 2 hours. The reaction temperature is maintained at 60°C
during the addition. The reaction mixture is further stirred at 60°C for 18 hours
after the addition before being cooled down to 25°C. Heptane (600 mL) is then
added and the reaction mixture is further stirred for 30 minutes before draining

the reactor. The precipitate is filtered off and washed with heptane (3x500 mL) and dried to yield 346 g (92% yield).

At this larger scale it was found important that the $\text{Al}(\text{Et})_2\text{Cl}$ was added gradually in the course of more than 1 hour, preferably between 1.5 and 3 hours to avoid excessive exothermic reactions and uncontrollable gas evolutions. Further the addition of heptane was beneficial to improve the precipitation of the product. Alternatives for heptane are alkanes, cycloalkanes, ethers such as MTBE.

Example 4

In this example step (c) of the process to prepare the complex according to the invention is illustrated.



400 mg of $[\text{Al}(3,4\text{-Py-Salphen})(\text{Cl})]$ complex (0.93 mmol) as obtained by a similar process as illustrated in Examples 1-3 was suspended in 5 mL toluene and 1 mL of dry DMF and 800 μL octyl bromide (4.6 mmol) was added. Heating the solution under a protective N_2 -atmosphere to 80 $^\circ\text{C}$, the complex fully dissolved and the solution changed from orange to a red slurry. After overnight reaction, the conversion was 37 % and an additional 2 mL octyl bromide was added to the reaction mixture and the heating was continued until the starting material was fully converted. The complex was isolated as DMF-complex with the overall formula $[\text{Al}(3,4\text{-Py-Salphen}(\text{N-Oct}))(\text{Cl})]\text{Br}(\text{DMF})_2$. Yield 480 mg, 63% yield.

The product was characterised by ^1H NMR (300 MHz, DMSO-d_6) δ 9.92 (s, 1H), 9.63 (s, 1H), 9.56 (s, 1H), 9.09 (d, $J = 6.9$ Hz, 1H), 8.69 (d, $J = 7.0$ Hz, 1H), 7.96 (s, 3H), 7.71 – 7.51 (m, 4H), 6.89 (t, $J = 7.6$ Hz, 2H), 4.61 (t, $J = 7.3$ Hz, 2H), 2.08 (br. 2H), 1.33 (br., 12H), 0.97 – 0.81 (m, 3H). The NMR data indicates that the desired product was formed.

Examples 1-4 illustrate the synthesis of the salen aluminium complex involving only 4 steps and having a high overall yield.

Example 5

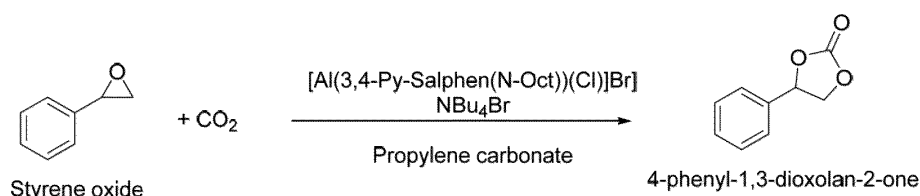
Example 4 is repeated except that instead of octyl bromide benzyl bromide was used resulting in a complex with the overall formula benzyl-containing catalyst $[\text{Al}(3,4\text{-Py-Salphen}(\text{N-Benzyl}))(\text{Cl})]\text{Br}$. The product was characterised by ^1H NMR (300 MHz, DMSO-d_6) δ 10.18 (s, 1H), 9.60 (s, 2H), 9.16 (d, $J = 6.9$ Hz, 1H), 8.69 (d, $J = 7.0$ Hz, 1H), 7.72 (s, 1H), 7.85 – 7.35 (m, 9H), 6.89 (td, $J = 7.7, 3.2$ Hz, 2H), 5.84 (s, 2H), 1.55 (d, $J = 4.6$ Hz, 18H). The NMR data indicates that the desired product was formed.

Example 5a

In a flame dried Schlenk is added $[\text{Al}(3,4\text{-Py-Salphen}(\text{Cl}))]$ complex (7.36 g, 15 mmol) and dried DMF (16.8 mL). The reaction is heated up to 80°C until all solids are dissolved before addition of 3-bromopropyltrimethoxysilane (11.3 mL, 60 mmol). The reaction is stirred at 80°C for 3 days before being cooled down. The resulting precipitate is filtered off and wash with Et_2O (3x20 mL) and dried to obtain 8.54 g of an orange solid (57% yield). The product was characterized by ^1H NMR (300 MHz, DMSO-d_6) δ 10.04 (s, 1H), 9.68 (s, 1H), 9.64 (s, 1H), 9.09 (d, $J = 6.9$ Hz, 1H), 8.74 (d, $J = 7.0$ Hz, 1H), 7.82 – 7.46 (m, 4H), 6.89 (t, $J = 7.6$ Hz, 2H), 4.58 (t, $J = 7.5$ Hz, 2H), 3.47 (s, 9H), 2.13 (p, $J = 7.9$ Hz, 2H), 0.77 – 0.53 (m, 2H).

Example 6

In this example the catalytic activity of the complex obtained in Example 4 is tested in the presence of added tetrabutylammonium bromide in the below reaction of styrene oxide and carbon dioxide to prepare 4-phenyl-1,3-dioxolan-2-one.



In a Schlenk reaction flask, 57.98 mg [Al(3,4-Py-Salphen(N-Oct))(Cl)]Br and 22.59 mg tetrabutylammonium bromide (TBAB) are charged and heated to 100 °C and put on vacuum. The flask was refilled with CO₂ gas after which the propylene carbonate (3.5 mL) and styrene oxide (1.0 mL) were added. The flask was purged with CO₂ and the stirring was started. The CO₂ partial pressure and total pressure at the start of the experiment was 0.106 MPa. After regular intervals, a sample was taken for analysis.

Substrate loading = 2.0 M

Catalyst loading = 0.8 mol%

Tetrabutylammonium bromide loading = 0.8 mol%

The conversion of styrene oxide and the formation of the styrene carbonate (4-phenyl-1,3-dioxolan-2-one) are listed in Table 1.

Example 7

In this example the catalytic activity of the complex obtained in Example 4 is tested in the absence of added tetrabutylammonium bromide in the reaction of styrene oxide and carbon dioxide to prepare 4-phenyl-1,3-dioxolan-2-one. Example 6 was repeated except that no tetrabutylammonium bromide was added. The conversion of styrene oxide and the formation of the styrene carbonate (4-phenyl-1,3-dioxolan-2-one) are listed in Table 1.

Example 8

Example 7 is repeated with the complex as prepared in Example 5: benzyl-containing catalyst [Al(3,4-Py-Salphen(N-Benzyl))(Cl)]Br. The conversion of styrene oxide and the formation of the styrene carbonate (4-phenyl-1,3-dioxolan-2-one) are listed in Table 1.

Example 9

Example 7 is repeated with the complex as prepared in Example 5: benzyl-containing catalyst [Al(3,4-Py-Salphen(N-Benzyl))(Cl)]Br. The conversion of styrene oxide and the formation of the styrene carbonate (4-phenyl-1,3-dioxolan-2-one) are listed in Table 1.

Comparative experiment A

Example 6 is repeated with a complex similar to the complex used in Example 6 except that the bridging group is a prior art phenylene bridging group. The conversion of styrene oxide and the formation of the styrene carbonate (4-phenyl-1,3-dioxolan-2-one) are listed in Table 1.

Comparative experiment B

Example 7 is repeated with a complex similar to the complex used in Example 7 except that the bridging group is a prior art phenylene bridging group. The conversion of styrene oxide and the formation of the styrene carbonate (4-phenyl-1,3-dioxolan-2-one) are listed in Table 1.

Table 1

Complex used of Example	Bridge	Added TBAB	Conversion styrene oxide after 2 hours	Production 4-phenyl-1,3-dioxolan-2-one after 2 hours (mmol)
6	Pyridinium group R= octyl	Yes	33.2	2.91
7	Pyridinium group R= octyl	No	14.7	1.29
8	Pyridinium group R= benzyl	Yes	45.5	3.98
9	Pyridinium group R= benzyl	No	14.4	1.26
A	Ph-bridge reference	Yes	19.0	1.66
B	Ph-bridge reference	No	1.8	0.15

The examples 6-9 show that the catalyst system according to this invention can be advantageously used as a catalyst or as part of a catalyst in a process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide. The results in Table 1 show that the conversion is higher when the reaction is performed in the presence of added tetrabutylammonium bromide. The results also show that the complex having the pyridinium bridging group has a catalytic activity in the absence of added tetrabutylammonium bromide. It is believed that the bromide anion associated with the pyridinium nitrogen acts as the co-catalyst. The results also show that the complex having

a pyridinium bridge is significantly more active than the prior art complex having a phenyl bridging group in the presence and absence of TBAB.

Example 10

5 0.020 mmol catalyst and 4.0 mmol maleic anhydride (MA) were placed in a flame dried Schlenk flask equipped with a stirring bar. The appropriate solvent (toluene, 1.0 mL) was added, followed by 4.0 mmol styrene epoxide (SO). The vial was sealed with a Teflon lined cap and placed in an aluminum heat block preheated to the desired temperature (65 °C – 80 °C). After the
10 reaction became viscous, the vial was removed from the heating block and a small aliquot was removed for ¹H NMR spectrum analysis to determine monomer conversion. The viscous reaction mixture was then dissolved in a minimum amount of dichloromethane and precipitated into an excess of hexanes. The solid was isolated and dried in vacuo. ¹H NMR confirmed the
15 formation of the unsaturated polyester. ¹H NMR (300 MHz, DMSO-d₆) δ 6.46 (m, 2H), 5.12 (m, 1H), 4.21 (m, 2H), 1.23 (d, J = 6.6 Hz, 3H).

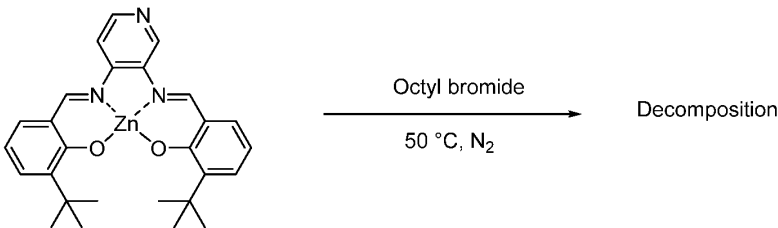
 The example was repeated with different catalyst loadings at different temperatures. The results are listed in Table 2, where conv (%) is the monomer
20 conversion, MW is the molecular weight of the polyester and Mn/Mw is the molar mass distribution/ polydispersity of the polyester.

Table 2

Epoxide	Temp (°C)	Amount (mmol)	Time (h)	MA (mmol)	PO (mmol)	Conv. (%)	MW (x10 ³)	Mn/Mw
PO	65	0.020	24	4.0	4.0	74	3.3	1.4
PO	65	0.010	24	4.0	4.0	66	2.3	1.4
PO	65	0.005	24	4.0	4.0	29	1.7	1.1
PO	80	0.020	24	4.0	4.0	91	4.3	1.2
PO	80	0.010	24	4.0	4.0	93	5.2	1.6
PO	80	0.005	24	4.0	4.0	81	5.0	1.6

Comparative experiment C

5 Alkylation of a zinc complex as below has been attempted with octyl bromide.



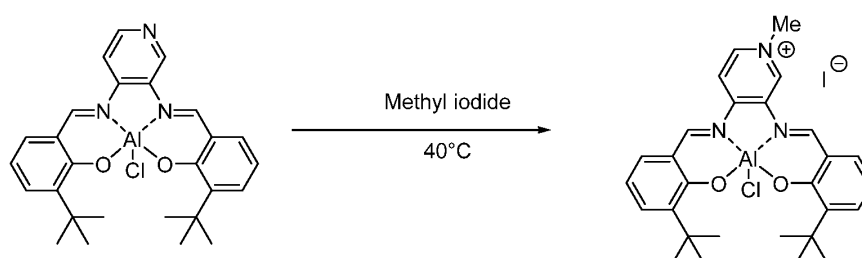
Experiments C1-C10 have been performed for the alkylation of the [Zn(3,4-Py-Salphen)] using octyl bromide wherein different solvent mixtures have been tested as listed in Table 3. It was found that the alkylation of the [Zn(3,4-Py-Salphen)] using octyl bromide gave no reactivity or decomposition of the [Zn(3,4-Py-Salphen)]. It was thus not possible to alkylate the [Zn(3,4-Py-Salphen)] with octyl bromide in a similar way as the [Al(3,4-Py-Salphen)(Cl)] in Example 4.

Table 3

Exp. nr	Al-complex	Octyl bromide (mL)	Solvent 1	amount	Solvent 2	amount	Total solvent
C1	200 mg	1.05	THF	4			4
C2	200 mg	1.05	Acetone	4			4
C3	200 mg	1.05	DMF	4			4
C4	200 mg	1.05	DMSO	4			4
C5	200 mg	1.05	Sulfolane	4			4
C6	200 mg	1.05	MeCN	4			4
C7	200 mg	1.05	THF	2	Acetone	2	4
C8	200 mg	1.05	MeCN	2	DMSO	2	4
C9	200 mg	1.05	MeCN	2	Toluene	2	4
C10	200 mg	1.05	MeOH	4			4

Example 11

5 In this example step (c) of the process to prepare the complex according to the invention is illustrated starting from of [Al(3,4-Py-Salphen)(Cl)] using methyl iodide as the halogen-R compound as shown below:



10 The [Al(3,4-Py-Salphen)(Cl)] complex (200 mg, 0.41 mmol, 1.0 eq) in DMF (4 mL) yielding a red solution. To this solution, methyl iodide (1 mL, 3.08 mmol, 7.5 eq) was added and the reaction mixture was heated to 40 °C for 20 hours.

After this reaction time, the reaction mixture was added to isopropyl acetate (40 mL) giving a red precipitate, which was separated. The solid was washed with isopropyl acetate (3x5 mL) and dried in the vacuum oven (40 °C, 5 mbar, 16 hours). Product was isolated as a red powder (231.5 mg, 89%). ¹H-NMR confirms formation of product. ¹H NMR (300 MHz, DMSO-*d*₆) δ 9.80 (d, *J* = 1.4 Hz, 1H), 9.60 (s, 1H), 9.48 (s, 1H), 8.99 (dd, *J* = 7.0, 1.3 Hz, 1H), 8.66 (d, *J* = 7.1 Hz, 1H), 7.65-7.54 (m, 2H), 6.89 (t, *J* = 7.6 Hz, 1H), 4.38 (s, 2H), 1.55 (d, *J* = 3.9 Hz, 18H).

Example 12

The [Al(3,4-Py-Salphen(N-Me))(Cl)]I complex as prepared in Example 11 has been tested at low CO₂ partial pressures. The other reaction conditions were as described in the earlier referred to article of ANTONELLO DECORTES ET AL: "Ambient Fixation of Carbon Dioxide using a Zn(II) salphen Catalyst", CHEMCATCHEM, JOHN WILEY & SONS, INC; HOBOKEN, USA, part 3, nr. 5, 2 March 2011 (2011-03-02), pages 831-834, XP072430479, ISSN: 1867-3880, DOI: 10.1002/CCTC.201100031. In table 4 Experiment D is the result from Table 2 of this article.

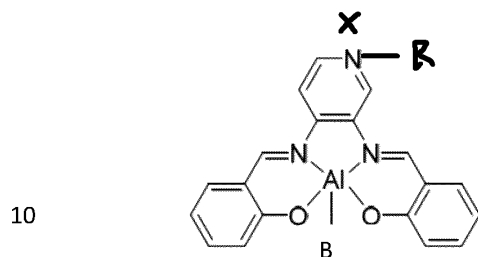
Table 4

Exp No.	Epoxide	Catalyst (A)	Solvent	Reaction time (h)	Yield (%)	Pressure CO ₂ (MPa)
D	Hexene oxide	[Zn(3,4-Py-Salphen(N-Me))]I	DCM	20.0	<1	1.0
12a	Hexene oxide	[Al(3,4-Py-Salphen(N-Me))(Cl)]I	DCM	16.0	3.0	0.1
12b	Styrene oxide	[Al(3,4-Py-Salphen(N-Me))(Cl)]I	DCM	3.0	4.0	0.1
12c	Styrene oxide	[Al(3,4-Py-Salphen(N-Me))(Cl)]I	DCM	69.0	17.0	0.1

CLAIMS

1. Optionally substituted salen aluminium complex having the following general formula:

5



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wherein B is a halogen, alkoxy or alkyl group and wherein the phenyl groups of the salen aluminium complex are optionally substituted, where R is a hydrocarbon group and X is a halogen anion.

15

2. Optionally substituted salen aluminium complex according to claim 1, wherein X is a iodide anion or a bromide anion.

20

3. Optionally substituted salen aluminium complex according to any one of claims 1-2, wherein R is a anchoring group to anchor the salen aluminium complex to a heterogeneous support.

25

4. Optionally substituted salen aluminium complex according to claim 3, wherein the anchoring group is an alkyl(trialkoxy) silane.

5. Aluminium complex according to claim 4, wherein the aluminium complex is [Al(3,4-Py-Salphen(N-Propyl(trimethoxy)silane))(Cl)]Br optionally substituted at the 3-position of the phenyl groups of the salphen structure.

30

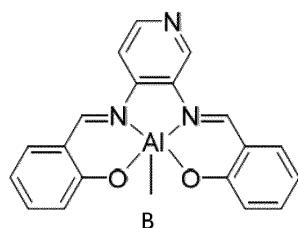
6. Supported complex wherein an aluminium complex according to any one of claims 1-5 is immobilized on the surface of a silica, alumina and/or silica alumina particle by means of the anchoring group R.

7. Catalyst system comprising a complex according to any one of claims 1 to 5 or a supported aluminium complex according to claim 6 and a bromide salt or a iodide salt as a co-catalyst.

5 8. Catalyst system according to claim 7, wherein the bromide salt is a quaternary ammonium bromide salt or a phosphonium bromide salt and the iodine salt is a quaternary ammonium iodide salt or a phosphonium iodide salt .

9. Optionally substituted salen aluminium intermediate complex:

10



15

wherein B is a halogen, alkoxy or alkyl group and wherein the phenyl groups of the salen aluminium complex are optionally substituted.

10. Process to prepare an optionally substituted salen aluminium intermediate complex according to claim 9 starting from a corresponding optionally substituted salen nickel or zinc complex having a pyridine bridging group , wherein the following steps are performed:

20 (a) demetallizing the corresponding optionally substituted salen nickel or zinc complex to obtain a demetallized salen ligand, and

25 (b) contacting the demetallized salen ligand of step (a) with an aluminium compound to obtain the optionally substituted salen aluminium intermediate complex.

11. Process according to claim 10, wherein in step (b) the demetallized salen ligand of step (a) is contacted with diethylaluminium chloride ($\text{Al}(\text{Et})_2\text{Cl}$) as the aluminium compound.

30

12. Process according to any one of claims 10-11, wherein in step (a) the corresponding substituted salen nickel or zinc ligand is demetallized in a water free demetallation process in the presence of imidazole in acetonitrile or imidazole in toluene.
- 5
13. Process according to any one of claims 10-12, wherein in a step (c) the optionally substituted salen aluminium intermediate complex having a 3-pyridine bridge is subjected to an alkylation to obtain the corresponding optionally substituted salen aluminium complex having a 3-pyridinium bridging group.
- 10
14. Process to prepare an optionally substituted salen aluminium intermediate complex according to any one of claims 1-5 starting from an optionally substituted salen aluminium intermediate complex according to claim 9, wherein the optionally substituted salen aluminium intermediate complex is subjected to an alkylation to obtain the optionally substituted salen aluminium intermediate complex according to any one of claims 1-5.
- 15
15. Use of the catalyst system according to any one of claims 7-8 as a catalyst or as part of a catalyst in a process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide.
- 20
16. Process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide in the presence of a catalyst system according to any one of claims 7-8 at a pressure of between 0.1 and 0.3 MPa.
- 25
17. Process according to claim 16, wherein X is a bromide ion and the catalyst system comprises the bromide salt co-catalyst.
- 30
18. Process according to any one of claims 16-17, wherein the carbon dioxide is contacted with the epoxide compound in a liquid also comprising the catalyst system, wherein the liquid is the cyclic carbonate.

19. Process according to claim 18, wherein the catalyst system is a supported aluminium complex according to claim 6 and wherein the resulting reaction mixture is a suspension.
- 5 20. Process according to any one of claims 16-19, wherein the epoxide compound has 2 to 8 carbon atoms.
21. Process according to claim 20, wherein the epoxide compound is ethylene oxide, propylene oxide, butylene oxide, pentene oxide, glycidol, styrene oxide, 10 epichlorohydrin or fluoroethylene oxide.