

SYNTHESIS OF CYCLIC CARBONATES

The present invention relates to a process for synthesising cyclic carbonates from epoxides and carbon dioxide using aluminium(salen) complexes as catalysts. The invention also provides novel aluminium(salen) complexes, and their synthesis.

Cyclic carbonates are commercially important products currently manufactured on a multi-tonne scale for use as polar aprotic solvents, additives, antifoam agents for anti-freeze, plasticisers, and monomers for polymer synthesis (see Darensbourg, *et al.*, *Coord. Chem. Rev.*, **153** (1996), 155-174; Coates, *et al.*, *Angew. Chem. Int. Ed.*, **43** (2004), 6618-6639).

The synthesis of cyclic carbonates generally involves the reaction of epoxides with carbon dioxide, and hence could be used to sequestrate carbon dioxide, thus reducing the level of greenhouse gases in the atmosphere.

Catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide are known in the art (see Darensbourg, *et al.*, *Coord. Chem. Rev.*, **153** (1996), 155-174; Yoshida, *et al.*, *Chem. Eur. J.*, **10** (2004), 2886-2893; Sun, *et al.*, *J. Organomet. Chem.*, **690** (2005), 3490-3497) although these require elevated reaction temperatures and / or high pressures of carbon dioxide, the reaction often being conducted in supercritical carbon dioxide (see Lu, *et al.*, *App. Cat. A*, **234** (2002), 25-33).

Ratzenhofer, *et al.*, (*Angew. Chemie Int. Ed. Engl.*, **19** (1980), 317-318) succeeded in carrying out the reaction between 2-methyloxirane and carbon dioxide at room temperature and atmospheric pressure using catalysts consisting of a mixture of a metal halide and a Lewis base. However, a long reaction time of 7 days was required. Kisch, *et al.*, (*Chem. Ber.*, **119** (1986), 1090-1094), carrying out the same reaction under the same conditions and also using catalysts of this type, reports a reaction time of 3.5 to 93 hours using up to 4 mol% of a ZnCl_2 catalyst and up to 16 mol% of a $(n\text{Butyl})_4\text{NI}$ catalyst.

Lu, *et al.*, (*J. Mol. Cat. A*, **210** (2004), 31-34; *J. Cat.*, **227** (2004), 537-541) describe the use of tetradentate Schiff-base aluminium complexes in conjunction with a quaternary ammonium salt or polyether-KY complexes as catalyst systems for the

reaction of various epoxides with carbon dioxide at room temperature and about 6 atmospheres.

5 Metal(salen) complexes, including aluminium(salen) complexes, are well-known in the art for their use as catalysts. Lu, *et al.*, *App. Cat. A*, **234** (2002), 25-33, describes the use of a monomeric aluminium(salen) catalyst.

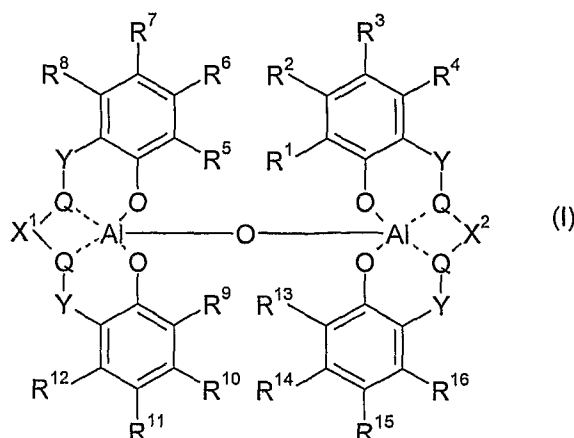
Also known in the art is the method of synthesising aluminium(salen) catalysts by treating a salen ligand with Me₃Al, Et₃Al, Me₂AlCl, Me₂AlOTf, Et₂AlBr or Et₂AlCl in a
10 two-stage process (reviewed in Atwood and Harvey, *Chem. Rev.*, 2001, **101**, 37-52).

The present inventor has previously found that, in the presence of a tetraalkylammonium halide cocatalyst, dimeric aluminium(salen) complexes are highly active catalysts for the reaction of epoxides with carbon dioxide to produce
15 cyclic carbonates, and allow the reaction to be carried out at room temperature and atmospheric pressure, using short reaction times and commercially viable amounts of catalyst, as described in Melendez, J., *et al.*, *Eur J. Inorg Chem*, **2007**, 3323-3326 and co-pending UK patent application No. 0708016.1, filed 25 April 2007, now published as WO 2008/132474.

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The present inventor has now found that it is possible to incorporate the co-catalyst required in this work into the catalyst molecule, so as to reduce or eliminate the amount of separate components needed. Furthermore, the present inventor has also found it is possible to immobilise the combined catalyst and co-catalyst on a solid
25 support.

Accordingly a first aspect of the invention provides a dimeric aluminium(salen) catalyst of formula I:



wherein:

Y-Q is $\text{CR}^{\text{C1}}=\text{N}$ or $\text{CR}^{\text{C1}}\text{R}^{\text{C2}}-\text{NR}^{\text{N1}}$, where R^{C1} , R^{C2} and R^{N1} are independently selected from H, halo, optionally substituted C_{1-20} alkyl, optionally substituted C_{5-20} aryl, ether and nitro;

each of the substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , and R^{16} , is independently selected from H, halo, optionally substituted C_{1-20} alkyl (including CAr_3 , where Ar is a C_{5-20} aryl group), optionally substituted C_{5-20} aryl, optionally substituted C_{3-20} heterocyclyl, ether and nitro;

X^1 and X^2 are independently either (i) a C_{2-5} alkylene chain, which is optionally substituted by one or more groups selected from C_{1-4} alkyl and C_{5-7} aryl, or a C_{1-3} bisoxyalkylene chain, which is optionally substituted by one or more groups selected from C_{1-4} alkyl and C_{5-7} aryl or (ii) represent a divalent group selected from C_{5-7} arylene, C_{5-7} cyclic alkylene and C_{3-7} heterocyclylene, which may be optionally substituted;

(i) (a) at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , and R^{16} is selected from L-A, where L is a single bond or a C_{1-10} alkylene group and A is an ammonium group paired with a counterion selected from Cl, Br and I; and/or

(b) at least one of X^1 and X^2 is a divalent C_{3-7} heterocyclene group, containing a ring atom which is a quaternary nitrogen atom paired with a counterion selected from Cl, Br and I; and/or

(c) at least one of X^1 and X^2 is a C_{2-5} alkylene chain or a C_{1-3} bisoxyalkylene chain, substituted by a group $-\text{Q}-\text{L}-\text{A}$, where Q is either $-\text{C}(=\text{O})-\text{O}-$, $-\text{C}(=\text{O})-\text{NH}-$, or a single bond;

and/or

- (ii) (a) one of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}$, and R^{16} is $L-A'$, where L is as defined above and A' is an ammonium linking group bound to a solid support and paired with a counterion selected from Cl, Br and I; or
- (b) one of X^1 and X^2 is a divalent C_{3-7} heterocyclene group, containing a ring atom which is a quaternary nitrogen forming part of an ammonium linking group bound to a solid support and paired with a counterion selected from Cl, Br and I; or
- (c) one of X^1 and X^2 is a C_{2-5} alkylene chain or a C_{1-3} bisoxyalkylene chain, substituted by a group $-Q-L-A'$.

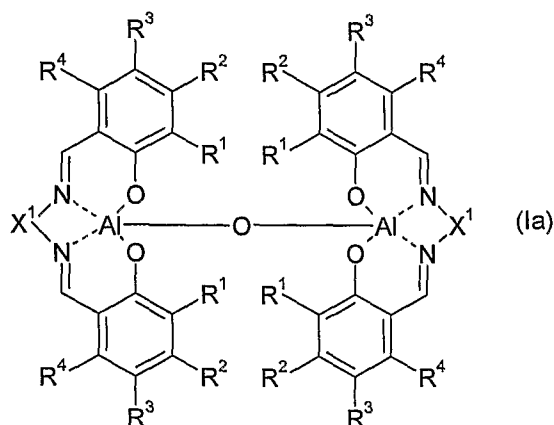
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Thus, when the catalyst is covalently bound to a solid support, only one linking group to the solid support is present. However, one or more ammonium groups/quaternary nitrogen atoms may be present.

- 15 The catalysts of formula I where: (a) at least one of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}$, and R^{16} is selected from $L-A$; and/or (b) at least one of X^1 and X^2 is a divalent C_{3-7} heterocyclene group, containing a ring atom which is a quaternary nitrogen atom paired with a counterion selected from Cl, Br and I; and/or
- (c) at least one of X^1 and X^2 is a C_{2-5} alkylene chain or a C_{1-3} bisoxyalkylene chain, substituted by a group $-Q-L-A$, where Q is either $-C(=O)-$ or a single bond, may be
- 20 immobilized on a solid support, either by the use of steric effects or by electrostatic binding.

- If the catalyst of formula I includes one or more chiral centres, then it may be a
- 25 (wholly or partially) racemic mixture or other mixture thereof, for example, a mixture enriched in one enantiomer or diastereoisomer, a single enantiomer or diastereoisomer, or a mixture of the stereoisomers. Methods for the preparation (e.g., asymmetric synthesis) and separation (e.g., fractional crystallisation and chromatographic means) of such isomeric forms are either known in the art or are
- 30 readily obtained by adapting the methods taught herein, or known methods, in a known manner. Preferably the catalyst of formula I is a single enantiomer, if a chiral centre is present.

The dimeric aluminium(salen) catalysts of the first aspect may be of formula Ia:

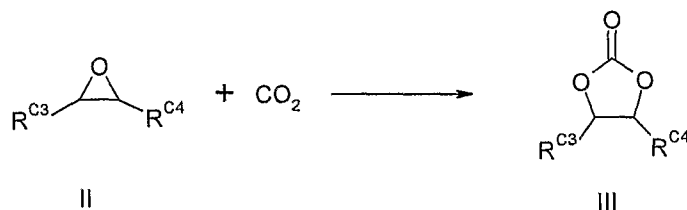


where R^1 , R^2 , R^3 , R^4 and X^1 are as defined above; and

- (a) at least one of R^1 , R^2 , R^3 and R^4 is selected from L-A, where L is a single bond or a C_{1-10} alkylene group and A is an ammonium group paired with a counterion selected from Cl, Br and I; and/or
- (b) X^1 is a divalent C_{3-7} heterocyclene group, containing a ring atom which is a quaternary nitrogen atom paired with a counterion selected from Cl, Br and I; or
- (c) X^1 is a C_{2-5} alkylene chain or a C_{1-3} bisoxyalkylene chain, substituted by a group -Q-L-A, where Q is either -C(=O)- or a single bond.

A second aspect of the present invention provides a process for the production of cyclic carbonates comprising contacting an epoxide with carbon dioxide in the presence of a dimeric aluminium(salen) catalyst according to the first aspect of the invention.

The reaction of the second aspect may be defined as follows:



wherein R^{C3} and R^{C4} are independently selected from H, optionally substituted C_{1-10} alkyl, optionally substituted C_{3-20} heterocyclyl and optionally substituted C_{5-20} aryl, or R^{C3} and R^{C4} form an optionally substituted linking group between the two carbon atoms to which they are respectively attached. The linking group, together with the carbon atoms to which it is attached, may form an optionally substituted C_{5-20} cycloalkyl or C_{5-20} heterocyclyl group. The C_{5-20} cycloalkyl or C_{5-20} heterocyclyl group may be substituted only in a single position on the ring, for example, adjacent the

epoxide. Suitable substituents, include optionally substituted C₁₋₁₀ alkyl, optionally substituted C₃₋₂₀ heterocyclyl and optionally substituted C₅₋₂₀ aryl.

A possible substituent for the C₁₋₁₀ alkyl group is a C₅₋₂₀ aryl group.

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The second aspect of the invention also provides the use of a dimeric aluminium(salen) catalyst of the first aspect of the invention for the production of cyclic carbonates from epoxides.

10 A third aspect of the invention provides a process for the synthesis of a dimeric aluminium(salen) catalyst of formula I.

Brief description of figure

Figure 1 shows a flow reactor for use with the catalysts of the present invention.

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Detailed description of the invention

Definitions

Epoxide: The term "epoxide", as used herein, may pertain to a compound of the formula:

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wherein R^{C3} and R^{C4} are independently selected from H, optionally substituted C₁₋₁₀ alkyl, optionally substituted C₃₋₂₀ heterocyclyl and optionally substituted C₅₋₂₀ aryl, or R^{C3} and R^{C4} form an optionally substituted linking group between the two carbon atoms to which they are respectively attached. The linking group, together with the carbon atoms to which it is attached, may form an optionally substituted C₅₋₂₀ cycloalkyl or C₅₋₂₀ heterocyclyl group. The C₅₋₂₀ cycloalkyl or C₅₋₂₀ heterocyclyl group may be substituted only in a single position on the ring, for example, adjacent the epoxide. Suitable substituents, include optionally substituted C₁₋₁₀ alkyl, optionally substituted C₃₋₂₀ heterocyclyl and optionally substituted C₅₋₂₀ aryl.

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The optional substituents may be selected from: C₁₋₁₀ alkyl, C₃₋₂₀ heterocyclyl, C₅₋₂₀ aryl, halo, hydroxy, ether, cyano, nitro, carboxy, ester, amido, amino, acylamido, ureido, acyloxy, thiol, thioether, sulfoxide, sulfonyl, thioamido and sulfonamino.

35 In some embodiments, the C₁₋₁₀ alkyl group is substituted by a C₅₋₂₀ aryl group.

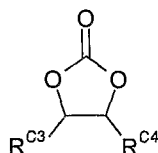
Preferably, the epoxide is a terminal epoxide, i.e. $R^{C4} = H$.

In some embodiments, R^{C3} is selected from optionally substituted C_{1-4} alkyl and
5 optionally substituted C_{5-7} aryl. In some of these embodiments R^{C3} is unsubstituted.

Preferred epoxides are ethylene oxide ($R^{C3} = R^{C4} = H$), propylene oxide ($R^{C3} =$
methyl, $R^{C4} = H$) butylene oxide ($R^{C3} =$ ethyl, $R^{C4} = H$), and styrene oxide ($R^{C3} =$
phenyl, $R^{C4} = H$).

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Cyclic carbonate: the term "cyclic carbonate", as used herein, may pertain to a
compound of the formula:



wherein R^{C3} and R^{C4} are as defined above.

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Solid support: Catalysts of the present invention may be immobilized on a solid
support by:

- (a) covalent binding (those where one of of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10},$
 $R^{11}, R^{12}, R^{13}, R^{14}, R^{15}$, and R^{16} is selected from L-A');
20 (b) steric trapping; or
- (c) electrostatic binding.

These various methods are reviewed by Carlos Baleizão and Hermenegildo Garcia in
"Chiral Salen Complexes: An Overview to Recoverable and Reusable Homogeneous
25 and Heterogeneous Catalysts" (*Chem. Rev.* 2006, **106**, 3987-4043).

For covalent binding, the solid support needs to contain or be derivatized to contain
reactive functionalities which can serve for covalently linking a compound to the
surface thereof. Such materials are well known in the art and include, by way of
30 example, silicon dioxide supports containing reactive Si-OH groups, polyacrylamide
supports, polystyrene supports, polyethyleneglycol supports, and the like. A further
example is sol-gel materials. Silica can be modified to include a 3-chloropropoxy
group by treatment with (3-chloropropyl)triethoxysilane. Another example is Al
pillared clay, which can also be modified to include a 3-chloropropoxy group by

treatment with (3-chloropropyl)triethoxysilane. Such supports will preferably take the form of small beads, pins/crowns, laminar surfaces, pellets or disks. They may also take the form of powders. Solid supports for covalent binding of particular interest in the present invention include siliceous MCM-41 and MCM-48 (modified with 3-aminopropyl groups), ITQ-2 and amorphous silica, SBA-15 and hexagonal mesoporous silica. Also of particular interest are sol-gels. Other conventional forms may also be used.

For steric trapping, the most suitable class of solid support is zeolites, which may be natural or modified. The pore size must be sufficiently small to trap the catalyst but sufficiently large to allow the passage of reactants and products to and from the catalyst. Suitable zeolites include zeolites X, Y and EMT as well as those which have been partially degraded to provide mesopores, that allow easier transport of reactants and products.

For the electrostatic binding of the catalyst to a solid support, typical solid supports may include silica, Indian clay, Al-pillared clay, Al-MCM-41, K10, laponite, bentonite, and zinc-aluminum layered double hydroxide. Of these silica and montmorillonite clay are of particular interest.

Alkyl: The term "alkyl", as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from a carbon atom of a hydrocarbon having from 1 to 20 carbon atoms (unless otherwise specified), which may be aliphatic or alicyclic and which may be saturated or unsaturated (e.g. partially saturated, fully unsaturated). Thus, the term "alkyl" includes the sub-classes alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, etc., as discussed below.

Alkylene: The term "alkylene", as used herein, pertains to a divalent moiety obtained by removing two hydrogen atoms from one or two carbon atoms of a hydrocarbon having from 1 to 20 carbon atoms (unless otherwise specified), which may be aliphatic or alicyclic and which may be saturated or unsaturated (e.g. partially saturated, fully unsaturated). Thus, the term "alkylene" includes the sub-classes alkenylene, alkynylene, cycloalkylene, cycloalkenylene, cycloalkynylene, etc., as discussed below.

In the context of alkyl and alkylene groups, the prefixes (e.g. C₁₋₄, C₁₋₇, C₁₋₂₀, C₂₋₇, C₃₋₇, etc.) denote the number of carbon atoms, or the range of number of carbon atoms.

For example, the term "C₁₋₄ alkyl", as used herein, pertains to an alkyl group having from 1 to 4 carbon atoms. Examples of groups of alkyl groups include C₁₋₄ alkyl

- 5 ("lower alkyl"), C₁₋₇ alkyl and C₁₋₂₀ alkyl. Note that the first prefix may vary according to other limitations; for example, for unsaturated alkyl groups, the first prefix must be at least 2; for cyclic alkyl groups, the first prefix must be at least 3; etc. For example, the term "C₁₋₇ alkylene", as used herein, pertains to an alkylene group having from 1 to 7 carbon atoms.

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Examples of (unsubstituted) saturated alkyl groups include, but are not limited to, methyl (C₁), ethyl (C₂), propyl (C₃), butyl (C₄), pentyl (C₅), hexyl (C₆), and heptyl (C₇).

- 15 Examples of (unsubstituted) saturated linear alkyl groups include, but are not limited to, methyl (C₁), ethyl (C₂), n-propyl (C₃), n-butyl (C₄), n-pentyl (amyl) (C₅), n-hexyl (C₆), and n-heptyl (C₇).

- Examples of (unsubstituted) saturated branched alkyl groups include iso-propyl (C₃), iso-butyl (C₄), sec-butyl (C₄), tert-butyl (C₄), iso-pentyl (C₅), and neo-pentyl (C₅).

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Examples of (unsubstituted) saturated alkylene groups include, but are not limited to, methylene (C₁), ethylene (C₂), propylene (C₃), butylene (C₄), pentylene (C₅), hexylene (C₆), and heptylene (C₇).

- 25 Examples of (unsubstituted) saturated linear alkylene groups include, but are not limited to, methylene (C₁), ethylene (C₂), n-propylene (C₃), n-butylene (C₄), n-pentylene (amylene) (C₅), n-hexylene (C₆), and n-heptylene (C₇).

- 30 Examples of (unsubstituted) saturated branched alkyl groups include iso-propylene (C₃), iso-butylene (C₄), sec-butylene (C₄), tert-butylene (C₄), iso-pentylene (C₅), and neo-pentylene (C₅).

- Alkenyl: The term "alkenyl", as used herein, pertains to an alkyl group having one or more carbon-carbon double bonds. Examples of groups of alkenyl groups include
- 35 C₂₋₄ alkenyl, C₂₋₇ alkenyl, C₂₋₂₀ alkenyl.

Examples of (unsubstituted) unsaturated alkenyl groups include, but are not limited to, ethenyl (vinyl, $-\text{CH}=\text{CH}_2$), 1-propenyl ($-\text{CH}=\text{CH}-\text{CH}_3$), 2-propenyl (allyl, $-\text{CH}_2-\text{CH}=\text{CH}_2$), isopropenyl (1-methylvinyl, $-\text{C}(\text{CH}_3)=\text{CH}_2$), butenyl (C_4), pentenyl (C_5), and hexenyl (C_6).

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Alkenylene: The term "alkenylene", as used herein, pertains to an alkylene group having one or more carbon-carbon double bonds. Examples of groups of alkenylene groups include C_{2-4} alkenylene, C_{2-7} alkenylene, C_{2-20} alkenylene.

- 10 Alkynyl: The term "alkynyl", as used herein, pertains to an alkyl group having one or more carbon-carbon triple bonds. Examples of groups of alkynyl groups include C_{2-4} alkynyl, C_{2-7} alkynyl, C_{2-20} alkynyl.

- 15 Examples of (unsubstituted) unsaturated alkynyl groups include, but are not limited to, ethynyl (ethinyl, $-\text{C}\equiv\text{CH}$) and 2-propynyl (propargyl, $-\text{CH}_2-\text{C}\equiv\text{CH}$).

Alkynylene: The term "alkynylene", as used herein, pertains to an alkylene group having one or more carbon-carbon triple bonds. Examples of groups of alkynylene groups include C_{2-4} alkynylene, C_{2-7} alkynylene, C_{2-20} alkynylene.

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- Cycloalkyl: the term "cycloalkyl", as used herein, pertains to an alkyl group which is also a cyclyl group; that is, a monovalent moiety obtained by removing a hydrogen atom from an alicyclic ring atom of a carbocyclic ring of a carbocyclic compound, which carbocyclic ring may be saturated or unsaturated (e.g. partially unsaturated, fully unsaturated), which moiety has from 3-20 carbon atoms (unless otherwise specified), including from 3 to 20 ring atoms. Thus, the term "cycloalkyl" includes the sub-classes cycloalkenyl and cycloalkynyl. Preferably, each ring has from 3 to 7 ring atoms. Examples of groups of cycloalkyl groups include C_{3-20} cycloalkyl, C_{3-15} cycloalkyl, C_{3-10} cycloalkyl, C_{3-7} cycloalkyl.

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- Cycloalkylene: the term "cycloalkylene", as used herein, pertains to an alkylene group which is also a cyclyl group; that is, a divalent moiety obtained by removing two hydrogen atoms from one or two alicyclic ring atoms of a carbocyclic ring of a carbocyclic compound, which carbocyclic ring may be saturated or unsaturated (e.g. partially unsaturated, fully unsaturated), which moiety has from 3-20 carbon atoms (unless otherwise specified), including from 3 to 20 ring atoms. Thus, the term

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“cycloalkylene” includes the sub-classes cycloalkenylene and cycloalkynylene. Preferably, each ring has from 3 to 7 ring atoms. Examples of groups of cycloalkylene groups include C₃₋₂₀ cycloalkylene, C₃₋₁₅ cycloalkylene, C₃₋₁₀ cycloalkylene, C₃₋₇ cycloalkylene.

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Cyclic alkylene: The term “cyclic alkylene” as used herein pertains to a divalent moiety obtained by removing a hydrogen atom from each of two adjacent alicyclic ring atoms of a carbocyclic ring of a carbocyclic compound, which carbocyclic ring may be saturated or unsaturated (e.g. partially saturated, fully unsaturated), which moiety has from 3 to 20 carbon atoms (unless otherwise specified), including from 3 to 20 ring atoms. Preferably each ring has from 5 to 7 ring atoms. Examples of groups of cyclic alkylene groups include C₃₋₂₀ cyclic alkylenes, C₃₋₁₅ cyclic alkylenes, C₃₋₁₀ cyclic alkylenes, C₃₋₇ cyclic alkylenes.

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Examples of cycloalkyl groups and cyclic alkylene groups include, but are not limited to, those derived from:

saturated monocyclic hydrocarbon compounds:

cyclopropane (C₃), cyclobutane (C₄), cyclopentane (C₅), cyclohexane (C₆), cycloheptane (C₇), methylcyclopropane (C₄), dimethylcyclopropane (C₅), methylcyclobutane (C₅), dimethylcyclobutane (C₆), methylcyclopentane (C₆), dimethylcyclopentane (C₇), methylcyclohexane (C₇), dimethylcyclohexane (C₈), menthane (C₁₀);

unsaturated monocyclic hydrocarbon compounds:

cyclopropene (C₃), cyclobutene (C₄), cyclopentene (C₅), cyclohexene (C₆), methylcyclopropene (C₄), dimethylcyclopropene (C₅), methylcyclobutene (C₅), dimethylcyclobutene (C₆), methylcyclopentene (C₆), dimethylcyclopentene (C₇), methylcyclohexene (C₇), dimethylcyclohexene (C₈);

saturated polycyclic hydrocarbon compounds:

thujane (C₁₀), carane (C₁₀), pinane (C₁₀), bornane (C₁₀), norcarane (C₇), norpinane (C₇), norbornane (C₇), adamantane (C₁₀), decalin (decahydronaphthalene) (C₁₀);

unsaturated polycyclic hydrocarbon compounds:

camphene (C₁₀), limonene (C₁₀), pinene (C₁₀);

polycyclic hydrocarbon compounds having an aromatic ring:

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indene (C₉), indane (e.g., 2,3-dihydro-1H-indene) (C₉), tetralin (1,2,3,4-tetrahydronaphthalene) (C₁₀), acenaphthene (C₁₂), fluorene (C₁₃), phenalene (C₁₃), acephenanthrene (C₁₅), aceanthrene (C₁₆), cholanthrene (C₂₀).

- 5 Heterocyclyl: The term "heterocyclyl", as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from a ring atom of a heterocyclic compound, which moiety has from 3 to 20 ring atoms (unless otherwise specified), of which from 1 to 10 are ring heteroatoms. Preferably, each ring has from 3 to 7 ring atoms, of which from 1 to 4 are ring heteroatoms.

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Heterocyclylene: The term "heterocyclylene", as used herein, pertains to a divalent moiety obtained by removing a hydrogen atom from each of two adjacent ring atoms of a heterocyclic compound, which moiety has from 3 to 20 ring atoms (unless otherwise specified), of which from 1 to 10 are ring heteroatoms. Preferably, each
15 ring has from 3 to 7 ring atoms, of which from 1 to 4 are ring heteroatoms.

The heterocyclyl or heterocyclylene group may be bonded via carbon or hetero ring atoms. Preferably, the heterocyclylene group is bonded via two carbon atoms.

- 20 When referring to heterocyclyl or heterocyclylene groups, the prefixes (e.g. C₃₋₂₀, C₃₋₇, C₅₋₆, etc.) denote the number of ring atoms, or range of number of ring atoms, whether carbon atoms or heteroatoms. For example, the term "C₅₋₆ heterocyclyl", as used herein, pertains to a heterocyclyl group having 5 or 6 ring atoms. Examples of groups of heterocyclyl groups include C₃₋₂₀ heterocyclyl, C₅₋₂₀ heterocyclyl, C₃₋₁₅
25 heterocyclyl, C₅₋₁₅ heterocyclyl, C₃₋₁₂ heterocyclyl, C₅₋₁₂ heterocyclyl, C₃₋₁₀ heterocyclyl, C₅₋₁₀ heterocyclyl, C₃₋₇ heterocyclyl, C₅₋₇ heterocyclyl, and C₅₋₆ heterocyclyl.

Similarly, the term "C₅₋₆ heterocyclylene", as used herein, pertains to a heterocyclylene group having 5 or 6 ring atoms. Examples of groups of

- 30 heterocyclylene groups include C₃₋₂₀ heterocyclylene, C₅₋₂₀ heterocyclylene, C₃₋₁₅ heterocyclylene, C₅₋₁₅ heterocyclylene, C₃₋₁₂ heterocyclylene, C₅₋₁₂ heterocyclylene, C₃₋₁₀ heterocyclylene, C₅₋₁₀ heterocyclylene, C₃₋₇ heterocyclylene, C₅₋₇ heterocyclylene, and C₅₋₆ heterocyclylene.

- 35 Examples of monocyclic heterocyclyl and heterocyclylene groups include, but are not limited to, those derived from:

N₁: aziridine (C₃), azetidine (C₄), pyrrolidine (tetrahydropyrrole) (C₅), pyrroline (e.g., 3-pyrroline, 2,5-dihydropyrrole) (C₅), 2H-pyrrole or 3H-pyrrole (isopyrrole, isoazole) (C₅), piperidine (C₆), dihydropyridine (C₆), tetrahydropyridine (C₆), azepine (C₇);

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O₁: oxirane (C₃), oxetane (C₄), oxolane (tetrahydrofuran) (C₅), oxole (dihydrofuran) (C₅), oxane (tetrahydropyran) (C₆), dihydropyran (C₆), pyran (C₆), oxepin (C₇);

S₁: thiirane (C₃), thietane (C₄), thiolane (tetrahydrothiophene) (C₅), thiane (tetrahydrothiopyran) (C₆), thiepane (C₇);

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O₂: dioxolane (C₅), dioxane (C₆), and dioxepane (C₇);

O₃: trioxane (C₆);

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N₂: imidazolidine (C₅), pyrazolidine (diazolidine) (C₅), imidazoline (C₅), pyrazoline (dihydropyrazole) (C₅), piperazine (C₆);

N₁O₁: tetrahydrooxazole (C₅), dihydrooxazole (C₅), tetrahydroisoxazole (C₅), dihydroisoxazole (C₅), morpholine (C₆), tetrahydrooxazine (C₆), dihydrooxazine (C₆), oxazine (C₆);

20

N₁S₁: thiazoline (C₅), thiazolidine (C₅), thiomorpholine (C₆);

N₂O₁: oxadiazine (C₆);

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O₁S₁: oxathiole (C₅) and oxathiane (thioxane) (C₆); and,

N₁O₁S₁: oxathiazine (C₆).

30

Examples of substituted (non-aromatic) monocyclic heterocyclyl and heterocyclylene groups include those derived from saccharides, in cyclic form, for example, furanoses (C₅), such as arabinofuranose, lyxofuranose, ribofuranose, and xylofuranse, and pyranoses (C₆), such as allopyranose, altropyranose, glucopyranose, mannopyranose, gulopyranose, idopyranose, galactopyranose, and talopyranose.

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C₅₋₂₀ aryl: The term "C₅₋₂₀ aryl", as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from an aromatic ring atom of a C₅₋₂₀ aromatic compound, said compound having one ring, or two or more rings (e.g., fused), and having from 5 to 20 ring atoms, and wherein at least one of said ring(s) is an aromatic ring. Preferably, each ring has from 5 to 7 carbon atoms.

The ring atoms may be all carbon atoms, as in "carboaryl groups" in which case the group may conveniently be referred to as a "C₅₋₂₀ carboaryl" group.

C₅₋₂₀ arylene: The term "C₅₋₂₀ arylene", as used herein, pertains to a divalent moiety obtained by removing a hydrogen atom from each of two adjacent ring atoms of a C₅₋₂₀ aromatic compound, said compound having one ring, or two or more rings (e.g., fused), and having from 5 to 20 ring atoms, and wherein at least one of said ring(s) is an aromatic ring. Preferably, each ring has from 5 to 7 carbon atoms.

The ring atoms may be all carbon atoms, as in "carboarylene groups" in which case the group may conveniently be referred to as a "C₅₋₂₀ carboarylene" group.

Examples of C₅₋₂₀ aryl and C₅₋₂₀ arylene groups which do not have ring heteroatoms (i.e. C₅₋₂₀ carboaryl and C₅₋₂₀ carboarylene groups) include, but are not limited to, those derived from benzene (i.e. phenyl) (C₆), naphthalene (C₁₀), anthracene (C₁₄), phenanthrene (C₁₄), and pyrene (C₁₆).

Alternatively, the ring atoms may include one or more heteroatoms, including but not limited to oxygen, nitrogen, and sulfur, as in "heteroaryl groups" or "heteroarylene groups". In this case, the group may conveniently be referred to as a "C₅₋₂₀ heteroaryl" or "C₅₋₂₀ heteroarylene" group, wherein "C₅₋₂₀" denotes ring atoms, whether carbon atoms or heteroatoms. Preferably, each ring has from 5 to 7 ring atoms, of which from 0 to 4 are ring heteroatoms.

The heteroaryl or heteroarylene group may be bonded via carbon or hetero ring atoms. Preferably, the heteroarylene group is bonded via two carbon atoms.

Examples of C₅₋₂₀ heteroaryl and C₅₋₂₀ heteroarylene groups include, but are not limited to, C₅ heteroaryl and C₅ heteroarylene groups derived from furan (oxole), thiophene (thiole), pyrrole (azole), imidazole (1,3-diazole), pyrazole (1,2-diazole),

triazole, oxazole, isoxazole, thiazole, isothiazole, oxadiazole, tetrazole and oxatriazole; and C₆ heteroaryl groups derived from isoxazine, pyridine (azine), pyridazine (1,2-diazine), pyrimidine (1,3-diazine; e.g., cytosine, thymine, uracil), pyrazine (1,4-diazine) and triazine.

5

Examples of C₅₋₂₀ heteroaryl and C₅₋₂₀ heteroarylene groups which comprise fused rings, include, but are not limited to, C₉ heteroaryl and C₉ heteroarylene groups derived from benzofuran, isobenzofuran, benzothiophene, indole, isoindole; C₁₀ heteroaryl and C₁₀ heteroarylene groups derived from quinoline, isoquinoline, benzodiazine, pyridopyridine; C₁₄ heteroaryl and C₁₄ heteroarylene groups derived from acridine and xanthene.

10

Bisoxyc₁₋₃ alkylene: -O-(CH₂)_m-O-, where m is 1 to 3.

The above alkyl, alkylene, cyclic alkylene, bisoxyalkylene, heterocyclyl, heterocyclylene, aryl, and arylene groups, whether alone or part of another substituent, may themselves optionally be substituted with one or more groups selected from themselves and the additional substituents listed below.

15

Halo: -F, -Cl, -Br, and -I.

20

Hydroxy: -OH.

Ether: -OR, wherein R is an ether substituent, for example, a C₁₋₇ alkyl group (also referred to as a C₁₋₇ alkoxy group), a C₃₋₂₀ heterocyclyl group (also referred to as a C₃₋₂₀ heterocyclyloxy group), or a C₅₋₂₀ aryl group (also referred to as a C₅₋₂₀ aryloxy group), preferably a C₁₋₇ alkyl group.

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Nitro: -NO₂.

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Cyano (nitrile, carbonitrile): -CN.

Acyl (keto): -C(=O)R, wherein R is an acyl substituent, for example, H, a C₁₋₇ alkyl group (also referred to as C₁₋₇ alkylacyl or C₁₋₇ alkanoyl), a C₃₋₂₀ heterocyclyl group (also referred to as C₃₋₂₀ heterocyclylacyl), or a C₅₋₂₀ aryl group (also referred to as C₅₋₂₀ arylacyl), preferably a C₁₋₇ alkyl group. Examples of acyl groups include, but are

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not limited to, $-\text{C}(=\text{O})\text{CH}_3$ (acetyl), $-\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ (propionyl), $-\text{C}(=\text{O})\text{C}(\text{CH}_3)_3$ (pivaloyl), and $-\text{C}(=\text{O})\text{Ph}$ (benzoyl, phenone).

Carboxy (carboxylic acid): $-\text{COOH}$.

5

Ester (carboxylate, carboxylic acid ester, oxycarbonyl): $-\text{C}(=\text{O})\text{OR}$, wherein R is an ester substituent, for example, a C_{1-7} alkyl group, a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group, preferably a C_{1-7} alkyl group. Examples of ester groups include, but are not limited to, $-\text{C}(=\text{O})\text{OCH}_3$, $-\text{C}(=\text{O})\text{OCH}_2\text{CH}_3$, $-\text{C}(=\text{O})\text{OC}(\text{CH}_3)_3$, and $-\text{C}(=\text{O})\text{OPh}$.

10

Amido (carbamoyl, carbamyl, aminocarbonyl, carboxamide): $-\text{C}(=\text{O})\text{NR}^1\text{R}^2$, wherein R^1 and R^2 are independently amino substituents, as defined for amino groups. Examples of amido groups include, but are not limited to, $-\text{C}(=\text{O})\text{NH}_2$, $-\text{C}(=\text{O})\text{NHCH}_3$, $-\text{C}(=\text{O})\text{N}(\text{CH}_3)_2$, $-\text{C}(=\text{O})\text{NHCH}_2\text{CH}_3$, and $-\text{C}(=\text{O})\text{N}(\text{CH}_2\text{CH}_3)_2$, as well as amido groups in which R^1 and R^2 , together with the nitrogen atom to which they are attached, form a heterocyclic structure as in, for example, piperidinocarbonyl, morpholinocarbonyl, thiomorpholinocarbonyl, and piperazinylcarbonyl.

15

Amino: $-\text{NR}^1\text{R}^2$, wherein R^1 and R^2 are independently amino substituents, for example, hydrogen, a C_{1-7} alkyl group (also referred to as C_{1-7} alkylamino or di- C_{1-7} alkylamino), a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group, preferably H or a C_{1-7} alkyl group, or, in the case of a "cyclic" amino group, R^1 and R^2 , taken together with the nitrogen atom to which they are attached, form a heterocyclic ring having from 4 to 8 ring atoms. Examples of amino groups include, but are not limited to, $-\text{NH}_2$, $-\text{NHCH}_3$, $-\text{NHCH}(\text{CH}_3)_2$, $-\text{N}(\text{CH}_3)_2$, $-\text{N}(\text{CH}_2\text{CH}_3)_2$, and $-\text{NHPh}$. Examples of cyclic amino groups include, but are not limited to, aziridinyl, azetidiny, pyrrolidinyl, piperidino, piperazinyl, perhydrodiazepinyl, morpholino, and thiomorpholino. In particular, the cyclic amino groups may be substituted on their ring by any of the substituents defined here, for example carboxy, carboxylate and amido.

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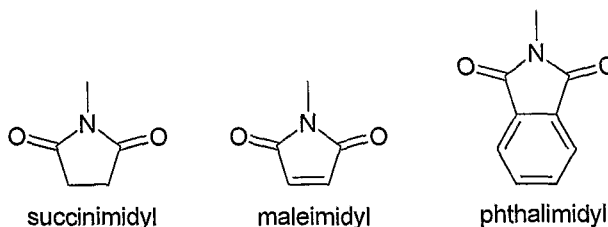
Ammonium: $-\text{NR}^{\text{N}1}\text{R}^{\text{N}2}\text{R}^{\text{N}3}$, wherein $\text{R}^{\text{N}1}$, $\text{R}^{\text{N}2}$ and $\text{R}^{\text{N}3}$ are independently ammonium substituents, for example, a C_{1-7} alkyl group, a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group and where one or two of $\text{R}^{\text{N}1}$, $\text{R}^{\text{N}2}$ and $\text{R}^{\text{N}3}$ may also be H. One of $\text{R}^{\text{N}1}$, $\text{R}^{\text{N}2}$ and $\text{R}^{\text{N}3}$ may be a C_{1-3} alkoxy ($-(\text{CH}_2)_{1-3}-\text{OH}$) group. Two or three of the ammonium substituents may join together to form cyclic or cage-like structures. Examples of

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ammonium groups include, but are not limited to, $-\text{NH}(\text{CH}_3)_2$, $-\text{NH}(\text{CH}(\text{CH}_3)_2)_2$, $-\text{N}(\text{CH}_3)_3$, $-\text{N}(\text{CH}_2\text{CH}_3)_3$, and $-\text{NH}_2\text{Ph}$.

- Ammonium linking group: $-\text{NR}^{\text{N}1}\text{R}^{\text{N}2}\text{R}^{\text{N}4}-$, wherein $\text{R}^{\text{N}1}$ and $\text{R}^{\text{N}2}$ are independently ammonium substituents, for example, a C_{1-7} alkyl group, a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group and where one or both of $\text{R}^{\text{N}1}$ and $\text{R}^{\text{N}2}$ may also be H. The two ammonium substituents may join together to form a cyclic structure. $\text{R}^{\text{N}4}$ is a divalent ammonium substituent, for example, a C_{1-7} alkylene group, a C_{3-20} heterocyclylene group, or a C_{5-20} arylene group or a divalent C_{1-3} alkyloxy ($-(\text{CH}_2)_{1-3}-\text{O}-$) group.
- Examples of ammonium linking groups include, but are not limited to, $-\text{NH}(\text{CH}_3)(\text{CH}_2)-$, $-\text{NH}(\text{CH}(\text{CH}_3)_2)(\text{C}(\text{CH}_3)_2)-$, $-\text{N}(\text{CH}_3)_2(\text{CH}_2)-$, $-\text{N}(\text{CH}_2\text{CH}_3)_2(\text{CH}_2\text{CH}_2)-$, and $-\text{NHPh}(\text{CH}_2)-$.

- Acylamido (acylamino): $-\text{NR}^1\text{C}(=\text{O})\text{R}^2$, wherein R^1 is an amide substituent, for example, hydrogen, a C_{1-7} alkyl group, a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group, preferably H or a C_{1-7} alkyl group, most preferably H, and R^2 is an acyl substituent, for example, a C_{1-7} alkyl group, a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group, preferably a C_{1-7} alkyl group. Examples of acylamide groups include, but are not limited to, $-\text{NHC}(=\text{O})\text{CH}_3$, $-\text{NHC}(=\text{O})\text{CH}_2\text{CH}_3$, and $-\text{NHC}(=\text{O})\text{Ph}$. R^1 and R^2 may together form a cyclic structure, as in, for example, succinimidyl, maleimidyl, and phthalimidyl:



- Ureido: $-\text{N}(\text{R}^1)\text{CONR}^2\text{R}^3$ wherein R^2 and R^3 are independently amino substituents, as defined for amino groups, and R^1 is a ureido substituent, for example, hydrogen, a C_{1-7} alkyl group, a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group, preferably hydrogen or a C_{1-7} alkyl group. Examples of ureido groups include, but are not limited to, $-\text{NHCONH}_2$, $-\text{NHCONHMe}$, $-\text{NHCONHEt}$, $-\text{NHCONMe}_2$, $-\text{NHCONEt}_2$, $-\text{NMeCONH}_2$, $-\text{NMeCONHMe}$, $-\text{NMeCONHEt}$, $-\text{NMeCONMe}_2$, $-\text{NMeCONEt}_2$ and $-\text{NHCONHPh}$.
- Acyloxy (reverse ester): $-\text{OC}(=\text{O})\text{R}$, wherein R is an acyloxy substituent, for example, a C_{1-7} alkyl group, a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group, preferably a C_{1-7} alkyl group. Examples of acyloxy groups include, but are not limited to, $-\text{OC}(=\text{O})\text{CH}_3$

(acetoxy), $-\text{OC}(=\text{O})\text{CH}_2\text{CH}_3$, $-\text{OC}(=\text{O})\text{C}(\text{CH}_3)_3$, $-\text{OC}(=\text{O})\text{Ph}$, $-\text{OC}(=\text{O})\text{C}_6\text{H}_4\text{F}$, and $-\text{OC}(=\text{O})\text{CH}_2\text{Ph}$.

Thiol : $-\text{SH}$.

5

Thioether (sulfide): $-\text{SR}$, wherein R is a thioether substituent, for example, a C_{1-7} alkyl group (also referred to as a C_{1-7} alkylthio group), a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group, preferably a C_{1-7} alkyl group. Examples of C_{1-7} alkylthio groups include, but are not limited to, $-\text{SCH}_3$ and $-\text{SCH}_2\text{CH}_3$.

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Sulfoxide (sulfinyl): $-\text{S}(=\text{O})\text{R}$, wherein R is a sulfoxide substituent, for example, a C_{1-7} alkyl group, a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group, preferably a C_{1-7} alkyl group. Examples of sulfoxide groups include, but are not limited to, $-\text{S}(=\text{O})\text{CH}_3$ and $-\text{S}(=\text{O})\text{CH}_2\text{CH}_3$.

15

Sulfonyl (sulfone): $-\text{S}(=\text{O})_2\text{R}$, wherein R is a sulfone substituent, for example, a C_{1-7} alkyl group, a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group, preferably a C_{1-7} alkyl group. Examples of sulfone groups include, but are not limited to, $-\text{S}(=\text{O})_2\text{CH}_3$ (methanesulfonyl, mesyl), $-\text{S}(=\text{O})_2\text{CF}_3$, $-\text{S}(=\text{O})_2\text{CH}_2\text{CH}_3$, and 4-methylphenylsulfonyl (tosyl).

20

Thioamido (thiocarbamyl): $-\text{C}(=\text{S})\text{NR}^1\text{R}^2$, wherein R^1 and R^2 are independently amino substituents, as defined for amino groups. Examples of amido groups include, but are not limited to, $-\text{C}(=\text{S})\text{NH}_2$, $-\text{C}(=\text{S})\text{NHCH}_3$, $-\text{C}(=\text{S})\text{N}(\text{CH}_3)_2$, and $-\text{C}(=\text{S})\text{NHCH}_2\text{CH}_3$.

25

Sulfonamino: $-\text{NR}^1\text{S}(=\text{O})_2\text{R}$, wherein R^1 is an amino substituent, as defined for amino groups, and R is a sulfonamino substituent, for example, a C_{1-7} alkyl group, a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group, preferably a C_{1-7} alkyl group. Examples of sulfonamino groups include, but are not limited to, $-\text{NHS}(=\text{O})_2\text{CH}_3$, $-\text{NHS}(=\text{O})_2\text{Ph}$ and $-\text{N}(\text{CH}_3)\text{S}(=\text{O})_2\text{C}_6\text{H}_5$.

30

As mentioned above, the groups that form the above listed substituent groups, e.g. C_{1-7} alkyl, C_{3-20} heterocyclyl and C_{5-20} aryl, may themselves be substituted. Thus, the above definitions cover substituent groups which are substituted.

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C_{1-3} alkylene: $-(\text{CH}_2)_m-$, where m is 1 to 3.

Chemically Protected Forms

It may be convenient or desirable to prepare, purify, handle and/or use the active compound in a chemically protected form. The term "chemically protected form" is
5 used herein in the conventional chemical sense and pertains to a compound in which one or more reactive functional groups are protected from undesirable chemical reactions under specified conditions (e.g., pH, temperature, radiation, solvent, and the like). In practice, well known chemical methods are employed to reversibly
10 render unreactive a functional group, which otherwise would be reactive, under specified conditions. In a chemically protected form, one or more reactive functional groups are in the form of a protected or protecting group (also known as a masked or masking group or a blocked or blocking group). By protecting a reactive functional group, reactions involving other unprotected reactive functional groups can be performed, without affecting the protected group; the protecting group may be
15 removed, usually in a subsequent step, without substantially affecting the remainder of the molecule. See, for example, Protective Groups in Organic Synthesis (T. Green and P. Wuts; 3rd Edition; John Wiley and Sons, 1999).

Unless otherwise specified, a reference to a particular compound also includes
20 chemically protected forms thereof.

A wide variety of such "protecting," "blocking," or "masking" methods are widely used and well known in organic synthesis. For example, a compound which has two nonequivalent reactive functional groups, both of which would be reactive under
25 specified conditions, may be derivatized to render one of the functional groups "protected," and therefore unreactive, under the specified conditions; so protected, the compound may be used as a reactant which has effectively only one reactive functional group. After the desired reaction (involving the other functional group) is complete, the protected group may be "deprotected" to return it to its original
30 functionality.

For example, a hydroxy group may be protected as an ether (-OR) or an ester (-OC(=O)R), for example, as: a t-butyl ether; a benzyl, benzhydryl (diphenylmethyl), or trityl (triphenylmethyl) ether; a trimethylsilyl or t-butyldimethylsilyl ether; or an
35 acetyl ester (-OC(=O)CH₃, -OAc).

For example, an aldehyde or ketone group may be protected as an acetal ($R-CH(OR)_2$) or ketal ($R_2C(OR)_2$), respectively, in which the carbonyl group ($>C=O$) is converted to a diether ($>C(OR)_2$), by reaction with, for example, a primary alcohol. The aldehyde or ketone group is readily regenerated by hydrolysis using a large
 5 excess of water in the presence of acid.

For example, an amine group may be protected, for example, as an amide ($-NRCO-R$) or a urethane ($-NRCO-OR$), for example, as: a methyl amide ($-NHCO-CH_3$); a benzyloxy amide ($-NHCO-OCH_2C_6H_5$, $-NH-Cbz$); as a t-butoxy amide
 10 ($-NHCO-OC(CH_3)_3$, $-NH-Boc$); a 2-biphenyl-2-propoxy amide ($-NHCO-OC(CH_3)_2C_6H_4C_6H_5$, $-NH-Bpoc$), as a 9-fluorenylmethoxy amide ($-NH-Fmoc$), as a 6-nitroveratryloxy amide ($-NH-Nvoc$), as a 2-trimethylsilylethoxy amide ($-NH-Teoc$), as a 2,2,2-trichloroethoxy amide ($-NH-Troc$), as an allyloxy amide ($-NH-Alloc$), as a 2-(phenylsulphonyl)ethoxy amide ($-NH-Psec$); or, in suitable cases
 15 (e.g., cyclic amines), as a nitroxide radical ($>N-O\bullet$).

For example, a carboxylic acid group may be protected as an ester for example, as: a C_{1-7} -alkyl ester (e.g., a methyl ester; a t-butyl ester); a C_{1-7} -haloalkyl ester (e.g., a C_{1-7} -trihaloalkyl ester); a tri- C_{1-7} -alkylsilyl- C_{1-7} -alkyl ester; or a C_{5-20} -aryl- C_{1-7} -alkyl ester
 20 (e.g., a benzyl ester; a nitrobenzyl ester); or as an amide, for example, as a methyl amide.

For example, a thiol group may be protected as a thioether ($-SR$), for example, as: a benzyl thioether; an acetamidomethyl ether ($-S-CH_2NHC(=O)CH_3$).
 25

In particular application in the present invention is the protection of hydroxy and amino groups.

Catalysed reactions

30 In one aspect of the present invention, there is provided a process for the production of cyclic carbonates comprising contacting an epoxide with carbon dioxide in the presence of a dimeric aluminium(salen) catalyst of formula I.

This reaction has the advantage that it may be carried out at easily accessible
 35 temperatures of between 0 and 40°C and pressures of between 0.5 and 2 atm. The reaction may even be carried out at temperatures of between 0 and 140°C and

pressures of between 0.5 and 5 atm. Preferably, the reaction temperature lies between 20 and 30°C. Yields of over 50% may be achieved with short reaction times of 3 to 24 hours, using commercially viable amounts of catalyst, that is, from 0.1 to 10 mol%, preferably 0.1 to 2.5 mol%. In some cases, yields of over 70% or over 90% may be achieved under these conditions.

The reaction may also be carried out in a flow reactor, wherein the reaction is continuous.

In some embodiments, the carbon dioxide may be supplied heated, and in other embodiments, the reaction may be heated by a conventional or microwave system.

Catalysts

The embodiments and preferences expressed below may be combined with one another, where appropriate.

In some aspects of the invention, L is selected from a single bond and C₁₋₇ alkylene.

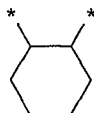
In some aspects of the invention, the aluminium(salen) catalyst of formula I is symmetrical, such that X¹=X², R¹=R¹³, R²=R¹⁴, R³=R¹⁵, R⁴=R¹⁶, R⁵=R⁹, R⁶=R¹⁰, R⁷=R¹¹, and R⁸=R¹². More preferably R¹, R⁵, R⁹, and R¹³ are identical, R², R⁶, R¹⁰ and R¹⁴ are identical, R³, R⁷, R¹¹, and R¹⁵ are identical, and R⁴, R⁸, R¹² and R¹⁶ are identical. Such catalysts are of formula Ia, which may be preferred.

If the catalyst is bound to a solid support, then it will not be fully symmetrical.

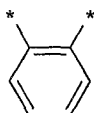
In some embodiments, X¹ and X² are the same.

In some embodiments, X¹ and X² are independently selected from a C₂₋₅ alkylene chain, which is preferably unsubstituted, and a C₁₋₃ bisoxylakylene chain, which is preferably unsubstituted. These groups can be represented as -(CH₂)_n- or -O-(CH₂)_p-O-, where n is 2, 3, 4, or 5 and p is 1, 2, or 3. In these embodiments, n is preferably 2 or 3 and p is preferably 1 or 2. n is more preferably 2. In these embodiments X¹ and X² are preferably selected from -(CH₂)_n- (e.g. -C₂H₄-).

- In other embodiments, X^1 and X^2 independently represent a divalent group selected from C_{5-7} arylene, C_{5-7} cyclic alkylene and C_{3-7} heterocyclylene, which may be optionally substituted. Preferably X^1 and X^2 independently represent C_{5-7} cyclic alkylene, and more preferably C_6 cyclic alkylene. This group is preferably saturated, and therefore is the group:



In other preferred embodiments, X^1 and X^2 independently represent C_{5-7} arylene, which is more preferably C_6 arylene, and in particular, benzylene:



10

- When X^1 and X^2 independently represent a divalent group selected from C_{5-7} arylene, C_{5-7} cyclic alkylene and C_{3-7} heterocyclylene, it may preferably be unsubstituted. If it is substituted, then the substituents may be selected from nitro, halo, C_{1-4} alkyl, including substituted C_{1-4} alkyl, (e.g. methyl, benzyl), C_{1-4} alkoxy (e.g. methoxy) and hydroxy.

15

Preferably Y-Q is $CR^{C1}=N$, wherein R^{C1} is as defined above. R^{C1} is preferably selected from H and C_{1-4} alkyl. More preferably Y-Q is $CH=N$.

- 20 If Y-Q is $CR^{C1}R^{C2}-NR^{N1}$, then in some embodiments R^{C1} , R^{C2} and R^{N1} are H.

Preferably $R^4 = R^8 = R^{12} = R^{16} = H$.

In some embodiments, $R^1 = R^5 = R^9 = R^{13} = H$.

25

- In some embodiments, it is one or more of R^3 , R^7 , R^{11} and R^{15} that is -L-A or L-A'. In some of these embodiments, if one of these groups is -L-A', the other groups are -L-A. Alternatively, the other groups may be -L-A^M, where A^M is a tertiary amine group, i.e. an amino group where the amino substituents are both not hydrogen, for example, C_{1-7} alkyl (ethyl). The L in all these groups may be the same.

30

Preferably those of R^1 , R^2 , R^3 , R^5 , R^6 , R^7 , R^9 , R^{10} , R^{11} , R^{13} , R^{14} , R^{15} and R^{16} which do not comprise -L-A or -L-A' are independently selected from H, C_{1-7} alkyl, ether and nitro.

- 5 If a group selected from R^1 , R^2 , R^3 , R^5 , R^6 , R^7 , R^9 , R^{10} , R^{11} , R^{13} , R^{14} , R^{15} and R^{16} is ether, then the ether group is preferably a C_{1-7} alkoxy group and more preferably C_{1-4} alkoxy group, e.g. methoxy.

- 10 If a group selected from R^1 , R^2 , R^3 , R^5 , R^6 , R^7 , R^9 , R^{10} , R^{11} , R^{13} , R^{14} , and R^{15} is C_{1-7} alkyl, it is preferably butyl, more preferably tert-butyl.

L is preferably unsubstituted.

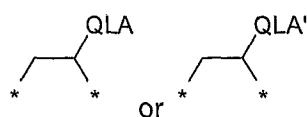
- 15 L may preferably be a C_{1-3} alkylene group, e.g. methylene, ethylene, propylene, and in some embodiments is methylene.

- 20 A may preferably be selected from ammonium groups where R^{N1} , R^{N2} and R^{N3} are independently selected from C_{1-7} alkyl groups and C_{5-20} aryl groups, and where one or two of R^{N1} , R^{N2} and R^{N3} may also be H. Ammonium groups of particular interest in the present invention include, but are not limited to, $-NH(CH_3)_2$, $-NH(CH(CH_3)_2)_2$, $-N(CH_3)_3$, $-N(CH_2CH_3)_3$, and $-NH_2Ph$.

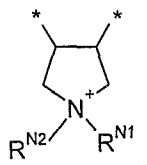
- 25 A' may preferably be selected from ammonium linking groups where R^{N1} and R^{N2} are independently selected from C_{1-7} alkyl groups and C_{5-20} aryl groups, where one or both of R^{N1} and R^{N2} may also be H and where R^{N4} is a C_{1-7} alkylene group. Ammonium linking groups of particular interest in the present invention include, but are not limited to, $-NH(CH_3)(CH_2)-$, $-NH(CH(CH_3)_2)(C(CH_3)_2)-$, $-N(CH_3)_2(CH_2)-$, $-N(CH_2CH_3)_2(CH_2CH_2)-$, and $-NHPh(CH_2)-$.

- 30 In some embodiments, Q may be $-C(=O)-O-$ or $-C(=O)-NH-$.

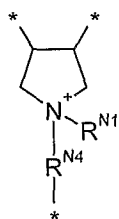
When X^1 and/or X^2 is substituted by -Q-L-A or -Q-L-A', it is preferably a C_2 or C_3 alkylene group, more preferably a C_2 alkylene group, and may be of the formula:



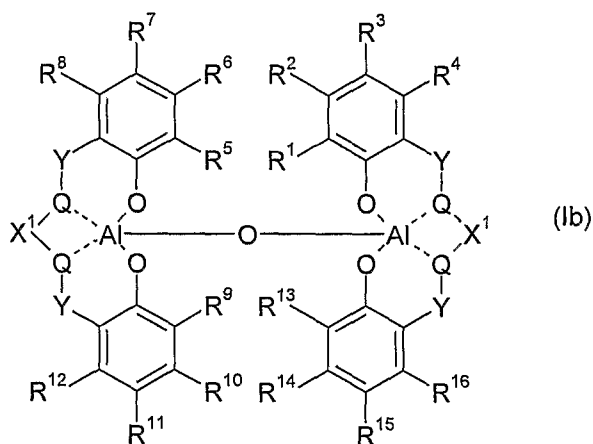
If X^1 or X^2 is a divalent C_{3-7} heterocyclene group containing a ring atom which is a quaternary nitrogen atom, then it is preferably of the formula:



- 5 If X^1 or X^2 is a divalent C_{3-7} heterocyclene group containing a ring atom which is a quaternary nitrogen forming part of an ammonium linking group, then it is preferably of the formula:



- 10 In some aspects of the present invention, the catalyst is of formula Ib:



wherein:

Y-Q is $CR^{C1}=N$ or $CR^{C1}R^{C2}-NR^{N1}$, where R^{C1} , R^{C2} and R^{N1} are independently selected from H, halo, optionally substituted C_{1-20} alkyl, optionally substituted C_{5-20} aryl, ether and nitro;

- 15 each of the substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , and R^{16} , is independently selected from H, halo, optionally substituted C_{1-20} alkyl (including CAr_3 , where Ar is a C_{5-20} aryl group), optionally substituted C_{5-20} aryl, optionally substituted C_{3-20} heterocyclyl, ether and nitro;

X is either of the formula $-(CH_2)_n-$ or $-O-(CH_2)_p-O-$, where n is 2, 3, 4, or 5 and p is 1, 2, or 3, or represents a divalent group selected from C_{5-7} arylene, C_{5-7} cyclic alkylene and C_{3-7} heterocyclylene, which may be optionally substituted;
at least one of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}$, and R^{16} is
5 selected from L-A, where L is a single bond or a C_{1-7} alkylene group and A is an ammonium group paired with a counterion selected from Cl, Br and I;
and/or one of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}$, and R^{16} is L-A', where L is as defined above and A' is a ammonium linking group bound to a solid support and paired with a counterion selected from Cl, Br and I.

10

The preferences expressed above also apply to the catalysts of formula Ib, where appropriate.

The reaction may be carried out under solvent-free conditions, depending on the
15 epoxides used. In some cases, the epoxides or the cyclic carbonates may act as a solvent for the catalyst. In particular, the inventors have found that propylene carbonate acts a suitable reaction solvent.

Some reactions may need the addition of a co-catalyst, Y^+ , and in particular MY,
20 where M is a suitable cation, such as onium halides, which include, but are not limited to, R_4NY , R_3SY , R_4PY and R_4SbY , where each R is independently selected from optionally substituted C_{1-10} alkyl, C_{3-20} heterocyclyl and C_{5-20} aryl groups and one R can be an acyl group, and simple halides, e.g. NaCl, KI.

25 It is preferred that the co-catalyst for this reaction is of the form R_4NY , where each R is independently C_{1-10} alkyl and Y is selected from I, Br and Cl. R is preferably selected from C_{3-5} alkyl, and more preferably is butyl. Y is preferably Br. Therefore, a particularly preferred co-catalyst is Bu_4NBr (TBAB). The amount of co-catalyst is preferably less than 2.5%, more preferably less than 1.0 mol% and most preferably
30 less than 0.5 mol%. In some embodiments, no separate co-catalyst is present.

Manufacture of dimeric aluminium(salen) complexes

In a third aspect of the invention, there is provided a process for the production of dimeric aluminium(salen) catalysts of formula I.

35

When the catalyst of formula I comprises one or more ammonium group paired with a counterion, it may be synthesised from a precursor comprising the corresponding ammonia groups by reaction with a organic halide (i.e. a C₁₋₇ alkyl, C₃₋₂₀ heterocyclyl or C₅₋₂₀ aryl halide), or an organic group with another leaving group (e.g. tosylate).

5

When the catalyst of formula I comprises an ammonium linking group bound to a solid support, it may be synthesised from a precursor catalyst comprising a corresponding ammonia group by reaction with a halide derived solid support or a solid support derivatized with another leaving group (e.g. tosylate).

10

Examples

General experimental methods

IR spectroscopy

IR spectra of liquids or of solids dissolved in a solvent were recorded between NaCl plates on a PE Spectrum 1 spectrometer. IR spectra of pure solids were recorded on a Nicolet380 FTIR spectrometer fitted with a 'Smart orbit' attachment.

15

NMR

All NMR spectra were recorded at ambient temperature on a Bruker Avance 300 spectrometer. The sample was dissolved in CDCl₃ unless specified otherwise.

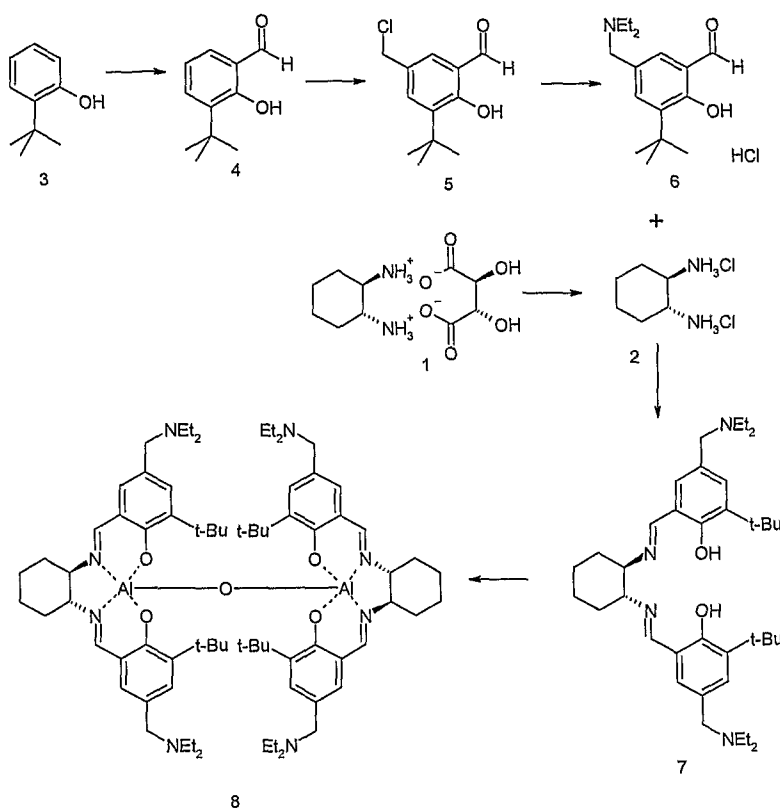
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Mass spectroscopy

Low resolution EI and CI spectra were recorded on a Varian Saturn 2200 GC-mass spectrometer. Low and high resolution electrospray spectra (ESI) were recorded on a Waters LCT Premier mass spectrometer.

25

Synthesis of Key Intermediates



(a) (1*R*,2*R*)-Cyclohexane-1,2-diammonium dichloride (2)

5 (Larrow, J. F, *et al.*, *J. Org. Chem.* **1994**, 59, 193)

To a suspension of (1*R*,2*R*)-cyclohexane-1,2-diammonium L-tartrate (1) (13.7 g, 52 mmol) in MeOH (50 mL) was added a cooled solution (0°C) of acetyl chloride (27.4 mL, 385 mmol) in MeOH (50 mL). The solution was stirred at room temperature overnight. The resulting precipitate was filtered off, washed with Et₂O (10 mL) and dried by suction to leave the desired product as a white powder. A second crop was obtained by diluting the mother liquor with Et₂O (200 mL) and cooling for half an hour. The product was collected and dried to yield a white powder. Yield: 80%. Crystalline white powder. $[\alpha]^{20}_D -16$ (c 5.0, aq. 1 M HCl). ¹H-NMR δ_H (DMSO-*d*₆): 1.05–1.25 (2H, m, CH₂CH₂CHN), 1.30–1.55 (2H, m, CH₂CH₂CHN), 1.60–1.75 (2H, m, CH₂CHN), 2.00–2.15 (2H, m, CH₂CHN), 3.13–3.30 (2H, m, CHN), 8.70 (6H, br s, NH₃).

(b) 3-*tert*-Butylsalicylaldehyde (4)

(Gisch, N.; Balzarini, J.; Meier, C. *J. Med. Chem.* **2007**, 50, 1658)

To a stirred suspension of 2-*tert*-butylphenol (3) (4.55g, 30 mmol), magnesium chloride (5.71 g, 60 mmol) and paraformaldehyde (2.08 g, 66 mmol) in THF (120 mL)

at room temperature, was added triethylamine (8.35 mL, 60 mmol) dropwise. The reaction was heated to reflux for 3 hours to give an orange suspension. This was extracted using EtOAc (3×50 mL). A small amount of diluted HCl can be added if a permanent emulsion is formed. The organic layers were dried over MgSO₄ and the volatiles evaporated under low pressure to yield a pale yellow oil which did not need any further purification. It can become dark green on storage. Yield: 90%. Pale yellow oil. ¹H-NMR δ_H: 1.44 (9H, s, 3×CH₃), 6.97 (1H, t, *J* = 7.5 Hz, H_{Ar}), 7.41 (1H, dd, *J* = 1.5 Hz, *J* = 7.5 Hz, H_{Ar}), 7.54 (1H, dd, *J* = 1.2 Hz, *J* = 7.5 Hz, H_{Ar}), 9.88 (1H, s, CHO), 11.82 (1H, s, OH).

(c) 3-*tert*-Butyl-5-chloromethylsalicylaldehyde (5)

A mixture of 3-*tert*-butylsalicylaldehyde (4) (3.56 g, 20 mmol) and paraformaldehyde (1.20 g, 40 mmol) was stirred with concentrated HCl (15 mL) for 14 days, although with the first drops of concentrated HCl, the emulsion became red. The mixture was then neutralized by treatment with a saturated solution of Na₂CO₃. The mixture was extracted with EtOAc (3×30 mL). Organic layers were dried over MgSO₄ and the volatiles were evaporated under low pressure to give a beige solid which did not require further purification. Yield: 97%. Beige to red solid. ¹H-NMR δ_H: 1.43 (9H, s, 3×CH₃), 4.59 (2H, s, CH₂), 7.43 (1H, d, *J* = 2.1 Hz, H_{Ar}), 7.52 (1H, d, *J* = 2.1 Hz, H_{Ar}), 9.87 (1H, s, CHO), 11.86 (1H, s, OH).

(d) 3-*tert*-Butyl-5-diethylaminomethylsalicylaldehyde hydrochloride (6)

To a solution of 3-*tert*-butyl-5-chloromethylsalicylaldehyde (5) (226.5 mg, 1 mmol) in acetonitrile (60 mL), diethylamine (1 mmol) was added dropwise to give a greenish solution. The reaction was stirred at 30°C overnight. After evaporation of volatiles, a green oil was obtained which was used without any purification for the next step. Yield: 77%. Green oil. ν_{max} 3300, 2899 and 1720 cm⁻¹. ¹H-NMR δ_H: 1.35 (9H, s, C(CH₃)₃), 1.45 (6H, t, *J* = 7.2 Hz, 2×CH₂CH₃), 3.43 (4H, q, *J* = 7.2 Hz, 2×CH₂CH₃), 4.90 (2H, s, CCH₂N), 7.57 (1H, d, *J* = 2.1 Hz, H_{Ar}), 8.03 (1H, d, *J* = 2.1 Hz, H_{Ar}), 9.98 (1H, s, CHO), 12.00 (1H, br s, OH). ¹³C-NMR δ_C(CDCl₃, 75 MHz): 10.8, 28.3, 33.7, 45.8, 56.0, 119.5, 129.8, 130.3, 133.7, 137.0, 159.0, 195.9.

HRMS: Calcd. for C₁₆H₂₆NO₂⁺ 264.1964, found 264.1953.

(e) (1*R*,2*R*)-*N,N'*-Bis(3-*tert*-butyl-5-diethylaminomethylsalicylidene)cyclohexane-1,2-diamine (7)

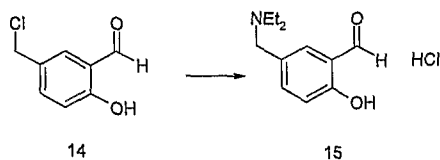
(1*R*,2*R*)-cyclohexane-1,2-diammonium dichloride (2)(93.5 mg, 0.5 mmol) and NaOMe (55 mg, 1 mmol) were stirred in MeOH (10 mL) for 30 min. Then, a solution
 5 of 3-*tert*-butyl-5-diethylaminomethylsalicylaldehyde hydrochloride (6)(299.8 mg, 1 mmol) in MeOH (5 mL) was added and the solution, which became rapidly yellow, was stirred overnight at 30°C. Evaporation of MeOH was followed by addition of a saturated solution of Na₂CO₃ (20 mL). Organic compounds were extracted using dichloromethane (3×15 mL). It is important that the aqueous phase remains
 10 completely colourless and that the organic layer changes colour from orange to green. Organic layers were dried over MgSO₄ and volatiles were removed under vacuum to give a greenish slurry oil which was used without any purification in the next step. Yield: 55%. Yellow-green oil. [α]_D²⁰ -184.5 (*c* 1.0, CHCl₃). $\nu_{\max}$ 3410, 2899, 1610, 1550 and 830 cm⁻¹. ¹H-NMR δ_{H} : 0.99 (12H, t, *J* = 7.2 Hz, 4×CH₂CH₃), 1.40
 15 (18H, s, 2×C(CH₃)₃), 1.50–2.05 (8H, m, (CH₂)₄), 2.44 (8H, q, *J* = 7.2 Hz, 4×CH₂CH₃), 3.40–3.50 (6H, m, 2×CHN, 2×CCH₂N), 6.95 (2H, d, *J* = 1.8 Hz, 2×H_{Ar}), 7.17 (2H, d, *J* = 1.8 Hz, 2×H_{Ar}), 8.28 (2H, s, 2×HC=N), 13.77 (2H, br s, 2×OH). ¹³C-NMR δ_{C} : 11.9, 24.4, 29.6, 33.2, 34.8, 46.8, 57.3, 72.5, 118.4, 128.8, 129.8, 130.1, 136.9, 159.3, 165.7. HRMS (ESI): Calcd. for C₃₈H₆₁N₄O₂⁺ 605.4795, found 605.4783.

20

(f) Bis[(1*R*,2*R*)-*N,N'*-Bis(3-*tert*-butyl-5-diethylaminomethylsalicylidene)cyclohexane-1,2-diaminoaluminium(III)] oxide (8)

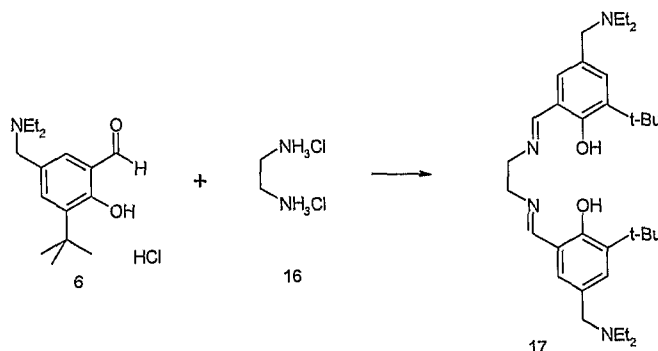
This reaction has to be performed under an inert atmosphere in dry conditions. Ligand (7)(1 mmol) and Al(OEt)₃ (324.1 mg, 2 mmol) were dissolved in toluene (10
 25 mL). The reacting mixture was heated to reflux for 5 hours. An occasional residue of alumina could be removed by filtering through a sinter. The mother liquor was evaporated and then, H₂O (30 mL) and dichloromethane (30 mL) were added. The complex was extracted using dichloromethane (3×20 mL) and organic layers were dried over MgSO₄. Volatiles were removed under low pressure to give a pale solid, which was recrystallised using acetonitrile. Yield: 40%. Pale green solid. [α]_D²⁰ -522
 30 (*c* 1.0, CHCl₃). $\nu_{\max}$ 2865, 1626, 1548, 1440, 1027, 836 and 577 cm⁻¹. ¹H-NMR δ_{H} : 1.02 (24H, t, *J* = 7.2 Hz, 8×CH₂CH₃), 1.46 (36H, s, 4×C(CH₃)₃), 1.50–2.15 (16H, m, 2×(CH₂)₄), 2.52–2.7 (16H, m, 8×CH₂CH₃), 3.10–3.15 (2H, m, 2×CHN), 3.50–3.60 (8H, m, 4×CCH₂N), 3.80–3.85 (2H, m, 2×CHN), 7.09 (4H, d, *J* = 5.7 Hz, 4×H_{Ar}), 7.35
 35 (4H, d, *J* = 5.7 Hz, 4×H_{Ar}), 8.19 (2H, s, 2×HC=N), 8.37 (2H, s, 2×HC=N). ¹³C-NMR δ_{C} : 10.2, 24.7, 29.9, 30.1, 35.0, 47.1, 57.6, 73.2, 118.9, 119.2, 128.9, 135.3, 141.7,

157.2, 165.1. m/z (ESI) 661.5 (100), 1275.9 (80), 1276.9 (72), 1277.9 (32), 1278.9 (16), 1279.9 (4)



5 (g) 5-Diethylaminomethylsalicylaldehyde 15

To a solution of 5-(chloromethyl)salicylaldehyde (14) (345 mg, 2 mmol) in acetonitrile (70 mL), diethylamine (0.21 mL, 2 mmol) was added and the mixture refluxed overnight. Then, the solvent was evaporated to give compound **15** (625 mg, 99%) as a yellow oil. $\nu_{\max}$ 3383, 2648 and 1653 cm^{-1} . $^1\text{H-NMR}$ δ_{H} 1.37 (6H, t, $J = 7.2$ Hz, $2 \times \text{CH}_2\text{CH}_3$), 3.43 (4H, q, $J = 7.2$ Hz, $2 \times \text{CH}_2\text{CH}_3$), 4.09 (2H, s, CCH_2N), 7.05 (1H, d, $J = 8.6$ Hz, H_{Ar}), 8.03 (1H, d, $J = 8.6$ Hz, H_{Ar}), 8.14 (1H, s, H_{Ar}), 9.98 (1H, s, CHO), 12.32 (1H, br s, OH). $^{13}\text{C-NMR}$ δ_{C} 11.4, 46.4, 56.0, 118.8, 121.3, 136.7, 139.0, 162.7, 196.5. m/z (ESI) 208 (MH^+ , 100), 293 (30), 317 (10). HRMS (ESI): Calculated for M^+ ($\text{C}_{12}\text{H}_{17}\text{NO}_2$) 208.1338, found 208.1355.

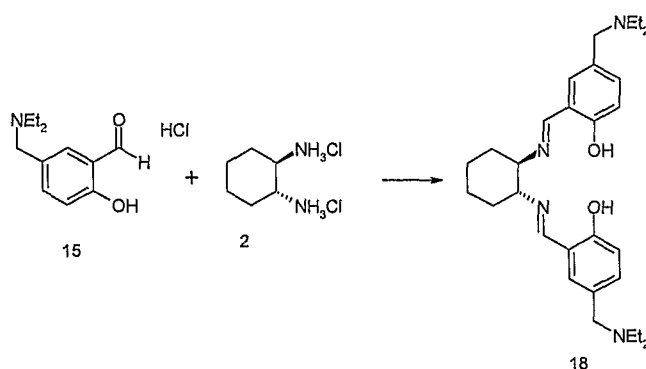


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(h) *N,N'*-Bis(3-*tert*-butyl-5-diethylaminomethylsalicylidene)ethane-1,2-diamine 17

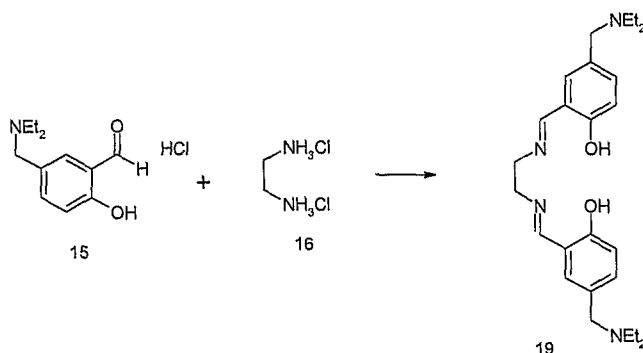
Compound 17 was synthesised from compounds 6 and 16 in an analogous manner to step (e) above. A yellow oil was obtained in 56% yield. $\nu_{\max}$ 2965, 2524 and 1629 cm^{-1} . $^1\text{H-NMR}$ δ_{H} 1.44 (12H, t $J = 7.5$ Hz, $4 \times \text{CH}_2\text{CH}_3$), 1.51 (18H, s, $2 \times \text{C}(\text{CH}_3)_3$), 2.70–2.80 (4H, m, CCH_2N), 3.02 (8H, q $J = 7.2$ Hz, $4 \times \text{CH}_2\text{CH}_3$), 3.60–3.80 (4H, m, $2 \times \text{CH}_2$), 7.07–7.35 (4H, m, $4 \times \text{H}_{\text{Ar}}$), 8.25 (2H, s, $2 \times \text{HC}=\text{N}$), 13.99 (2H, br s, $2 \times \text{OH}$). $^{13}\text{C-NMR}$ δ_{C} 10.4, 28.0, 33.3, 45.2, 55.7, 58.1, 116.8, 128.2, 128.8, 135.6, 157.7, 165.3, 165.8. m/z (ESI) 551 (MH^+ , 100), 524 (30). HRMS (ESI): Calculated for MH^+ ($\text{C}_{34}\text{H}_{55}\text{N}_4\text{O}_2$) 551.4325, found 551.4294.

25



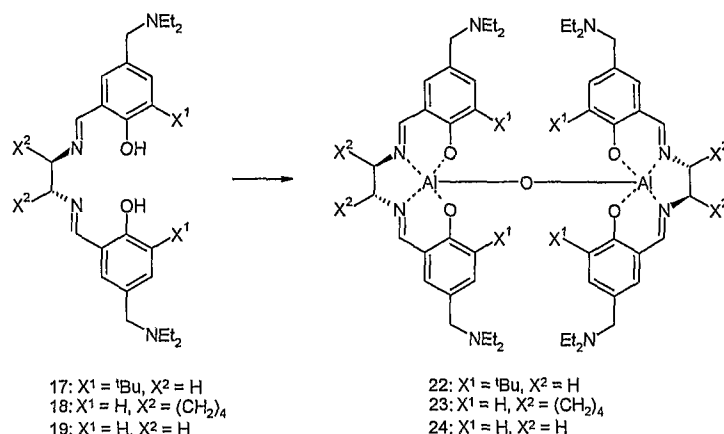
(i) (1*R*,2*R*)-*N,N'*-Bis(5-diethylaminomethylsalicylidene)cyclohexane-1,2-diamine 18

Compound 18 was synthesised from compounds 15 and 2 in an analogous manner to step (e) above. A yellow oil was obtained in 65% yield. $[\alpha]_D^{20}$ -302 (c 0.1, CHCl₃). $\nu_{\max}$ 2939, 1631 and 1089 cm⁻¹. ¹H-NMR δ_H 1.25 (12H, t J = 7.2 Hz, 4×CH₂CH₃), 1.50–2.00 (8H, m, (CH₂)₄) 2.89 (8H, q J = 7.6 Hz, 4×CH₂CH₃), 2.90–3.00 (4H, m, 2×CCH₂N), 3.90–4.00 (2H, m, 2×CH), 6.83 (2H, d J = 8.3 Hz, 2×H_{Ar}), 7.36 (2H, d J = 8.4 Hz, 2×H_{Ar}), 7.43 (2H, s, 2×H_{Ar}) 8.25 (2H, s, 2×HC=N), 13.40 (2H, br s, 2×OH). ¹³C-NMR δ_C 9.5, 24.4, 33.0, 46.9, 56.0, 72.6, 117.7, 118.9, 120.8, 134.3, 134.8, 161.4, 165.3. m/z (ESI) 493 (MH⁺, 100), 420 (20). HRMS (ESI): Calculated for MH⁺ (C₃₀H₄₅N₄O₂⁺) 493.3542, found 493.3544.



(j) *N,N'*-Bis(5-diethylaminomethylsalicylidene)ethane-1,2-diamine 19

Compound 19 was synthesised from compounds 15 and 16 in an analogous manner to step (e) above. A yellow oil was obtained in 53% yield. $\nu_{\max}$ 2801, 1632, and 1083 cm⁻¹. ¹H-NMR δ_H 1.21 (12H, t J = 7.5 Hz, 4×CH₂CH₃), 2.70–2.80 (4H, m, CCH₂N), 2.96 (8H, q J = 7.2 Hz, 4×CH₂CH₃), 3.85–3.95 (4H, m, 2×CH₂), 6.83 (2H, d J = 8.6 Hz, 2×H_{Ar}), 7.26 (2H, d J = 8.6 Hz, 2×H_{Ar}), 7.42 (2H, s, 2×H_{Ar}), 8.34 (2H, s, 2×HC=N), 13.21 (2H, br s, 2×OH). ¹³C-NMR δ_C 11.9, 43.5, 47.8, 57.2, 117.0, 129.6, 126.5, 130.4, 132.0, 133.4, 166.9. m/z (ESI) 439 (MH⁺, 100), 420 (20). HRMS (ESI): Calculated for MH⁺ (C₃₄H₅₅N₄O₂⁺) 439.3073, found 439.3090.



(k) Bis[*N,N'*-Bis(3-*tert*-butyl-5-diethylaminomethylsalicylidene)ethane-1,2-diaminoaluminium(III)] oxide 22, Bis[(1*R*,2*R*)-*N,N'*-Bis(5-

5 diethylaminomethylsalicylidene)cyclohexane-1,2-diaminoaluminium(III)] oxide 23 and Bis[*N,N'*-Bis(5-diethylaminomethylsalicylidene)ethane-1,2-diaminoaluminium(III)] oxide 24

Ligands 17-19 were converted to complexes 22-24 in an analogous manner to step (f) above.

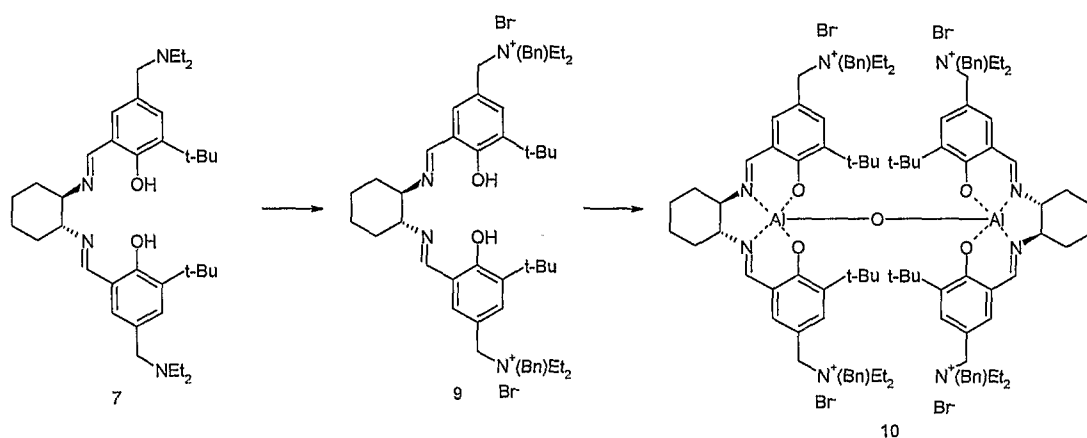
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22: pale yellow solid obtained in 55% yield. ν_{max} 2522 and 2159 cm^{-1} . $^1\text{H-NMR}$ δ_{H} 1.10–1.20 (24H, m, $8 \times \text{CH}_2\text{CH}_3$), 1.43 (36H, s, $4 \times \text{C}(\text{CH}_3)_3$), 2.90–3.15 (16H, m, $8 \times \text{CH}_2\text{CH}_3$), 3.50–3.60 (8H, m, $4 \times \text{CCH}_2\text{N}$), 3.70–4.00 (8H, m, $4 \times \text{CH}_2\text{N}$), 7.19 (4H, s, $4 \times \text{H}_{\text{Ar}}$), 7.30 (4H, s, $4 \times \text{H}_{\text{Ar}}$), 8.33 (4H, s, $4 \times \text{HC}=\text{N}$). $^{13}\text{C-NMR}$ δ_{C} 11.2, 24.2, 33.6, 46.5, 15 55.3, 55.9, 120.9, 135.5, 137.5, 137.8, 139.6, 140.9, 162.0. m/z (ESI) 1170 (10), 1169 (35), 1168 (90), 1167 (MH^+ , 100). HRMS (ESI): Calculated for MH^+ ($\text{C}_{68}\text{H}_{104}\text{N}_8\text{O}_5\text{Al}_2^+$) 1167.7839, found 1167.7799.

23: pale yellow solid obtained in 67% yield. $[\alpha]_{\text{D}}^{20} -170$ (c 0.01, DMSO). ν_{max} 2859, 20 1631 and 1084 cm^{-1} . $^1\text{H-NMR}$ δ_{H} (DMSO- d_6): 1.04–1.99 (24H, m, $8 \times \text{CH}_2\text{CH}_3$), 1.50–2.15 (16H, m, $2 \times (\text{CH}_2)_4$), 2.5–2.6 (16H, m, $8 \times \text{CH}_2\text{CH}_3$), 3.1–4.5 (12H, m, $4 \times \text{CHN} + 4 \times \text{CCH}_2\text{N}$), 6.91 (4H, d, $J = 7.6$ Hz, $4 \times \text{H}_{\text{Ar}}$), 7.40 (4H, d, $J = 7.6$ Hz, $4 \times \text{H}_{\text{Ar}}$), 7.55 (4H, s, $4 \times \text{H}_{\text{Ar}}$), 8.43 (4H, s, $4 \times \text{HC}=\text{N}$).

24: pale yellow solid obtained in 65% yield. ν_{max} 2971, 2225 and 1634 cm^{-1} . $^1\text{H-NMR}$ δ_{H} (DMSO- d_6): 1.05 (24H, m, $8 \times \text{CH}_2\text{CH}_3$), 2.15–3.5 (24H, m, $8 \times \text{CH}_2\text{CH}_3 + 4 \times \text{CCH}_2\text{N}$), 3.90 (8H, m, CH_2N), 6.81 (4H, d, $J = 5.7$ Hz, $4 \times \text{H}_{\text{Ar}}$), 7.32 (8H, m, $8 \times \text{H}_{\text{Ar}}$), 8.50 (4H, s, $\text{HC}=\text{N}$).

Example 1



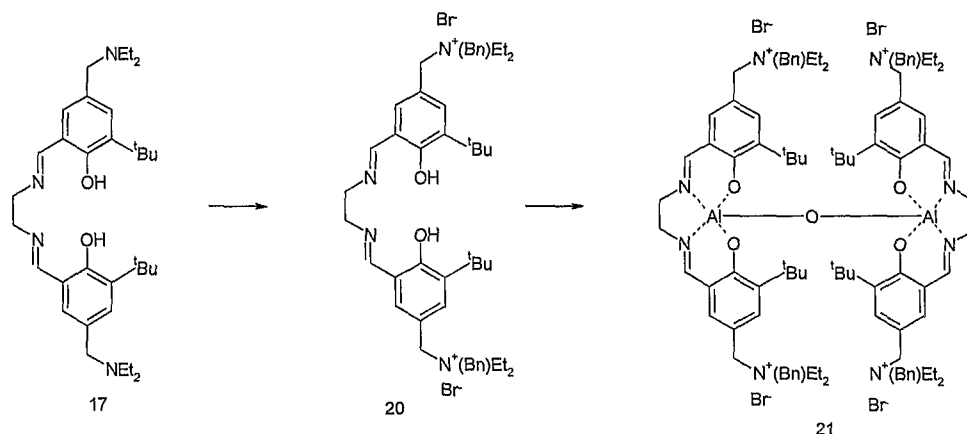
5 (a) **(1*R*,2*R*)-*N,N'*-Bis[3-*tert*-butyl-5-(*N*-benzyl-*N,N*-diethylaminomethyl)salicylidene]cyclohexane-1,2-diamine dibromide (9)**

To a solution of (1*R*,2*R*)-*N,N'*-bis(3-*tert*-butyl-5-diethylaminomethyl)salicylidene)-cyclohexane-1,2-diamine (7) (604.9 mg, 1 mmol) in acetonitrile (60 mL), benzyl bromide (342.1 mg, 2 mmol) was added dropwise to give a yellow solution. The
 10 reaction was stirred at 30°C overnight. After evaporation of volatiles, a yellow oil was obtained which was recrystallised from *n*-hexane. Yield: 55%. Bright yellow solid.
 $[\alpha]_D^{20} -38.6$ (*c* 1.0, CHCl_3). ν_{max} 3392, 2960, 1608, 1545 and 1470 cm^{-1} . $^1\text{H-NMR}$ δ_{H} : 1.00–2.00 (38H, m, 10 $\times$ CH₃, (CH₂)₄), 3.40–3.50 (2H, m, 2 $\times$ CHN), 3.56 (8H, q, *J* = 7.5 Hz, 4 $\times$ CH₂CH₃), 4.20 (4H, 2 $\times$ CCH₂N), 4.99 (4H, 2 $\times$ CCH₂N), 6.44 (2H, d, *J* = 2.4 Hz, 2 $\times$ H_{Ar}), 7.65 (2H, d, *J* = 2.4 Hz, 2 $\times$ H_{Ar}), 8.38 (2H, s, 2 $\times$ HC=N), 14.30 (2H, br s, 2 $\times$ OH). $^{13}\text{C-NMR}$ δ_{C} : 11.3, 23.4, 29.3, 31.2, 35.1, 51.1, 60.3, 60.4, 72.7, 120.2, 128.6,
 15 128.8, 129.2, 129.9, 130.6, 134.9, 157.2, 163.9.

20 (b) **Bis[(1*R*,2*R*)-*N,N'*-Bis(3-*tert*-butyl-5-(*N*-benzyl-*N,N*-diethylaminomethyl)salicylidene bromide]cyclohexane-1,2-diaminoaluminium(III) oxide (10)**

This reaction has to be performed under an inert atmosphere in dry conditions. Ligand (9) (1 mmol) and Al(OEt)₃ (324.1 mg, 2 mmol) were dissolved in a mixture of toluene (5 mL) and ethanol (5 mL). The reacting mixture was heated to reflux for 5 hours. An occasional residue of alumina could be removed by filtering through a
 25 sinter. The mother liquor was evaporated, then H₂O (30 mL) and dichloromethane (30 mL) were added. The complex was extracted using dichloromethane (3 $\times$ 20 mL) and organic layers were dried over MgSO₄. Volatiles were removed under low pressure to give a pale solid, which was recrystallised using Et₂O. Yield: 33%. Pale yellow solid. $[\alpha]_D^{20} -281$ (*c* 1.0, CHCl_3). IR 2946, 1624, 1551, 1470, 1208 and 1030

cm⁻¹. ¹H-NMR δ_H: 1.05 (24H, t, *J* = 7.3 Hz, 8×CH₂CH₃), 1.45 (36H, s, 4×C(CH₃)₃), 1.50–2.20 (16H, m, 2×(CH₂)₄), 2.45–2.50 (16H, m, 8×CH₂CH₃), 3.10–3.15 (2H, m, 2×CHN), 3.40–3.50 (16H, m, 8×CCH₂N), 3.80–3.85 (2H, m, 2×CHN), 7.10–7.50 (28H, m, 28×H_{Ar}), 8.20 (2H, s, 2×HC=N), 8.35 (2H, s, 2×HC=N). ¹³C-NMR δ_C: 10.3, 24.5, 30.0, 30.2, 34.6, 48.3, 57.6, 60.2, 73.8, 119.1, 119.6, 124.6, 127.4, 127.9, 128.9, 135.2, 141.6, 156.5, 166.1.

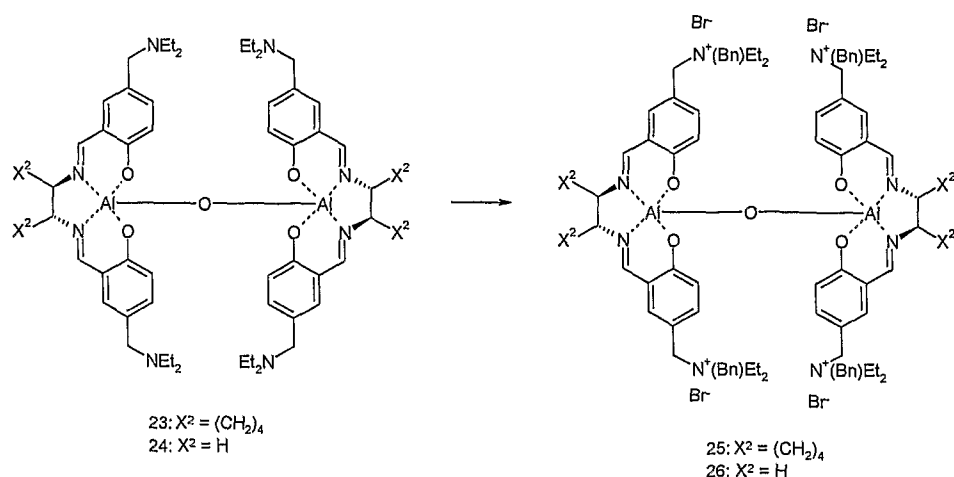


(c) ***N,N'*-Bis[3-*tert*-butyl-5-(*N*-benzyl-*N,N*-diethylaminomethyl)salicylidene]-ethane-1,2-diamine dibromide (20)**

The bis-ammonium salt (20) was synthesised from the salen ligand (17) in an analogous manner to step (a) above. $\nu_{\max}$ 3383, 2648 and 1647 cm⁻¹. ¹H-NMR δ_H 1.44 (12H, t *J* = 7.5 Hz, 4×CH₂CH₃), 1.51 (18H, s, 2×C(CH₃)₃), 2.78 (8H, q *J* = 7.2 Hz, 4×CH₂CH₃), 3.6–3.8 (4H, m, 2×CH₂N), 3.9–4.1 (4H, m, CCH₂N), 7.0–7.4 (4H, m, 4×H_{Ar}), 8.25 (2H, s, 2×HC=N), 13.99 (2H, br s, 2×OH). ¹³C-NMR δ_C 10.9, 29.6, 35.1, 46.5, 56.6, 59.7, 65.7, 118.8, 121.1, 127.5, 128.8, 129.0, 129.5, 135.5, 137.3, 139.6, 141.0, 162.6.

(d) **Bis[*N,N'*-Bis(3-*tert*-butyl-5-(*N*-benzyl-*N,N*-diethylaminomethyl)salicylidene)bromide]ethane-1,2-diaminoaluminium(III) oxide (21)**

The catalyst (21) was synthesised from the bis-ammonium salt (20) in an analogous manner to step (b) above. A pale yellow solid was obtained in 42% yield. $\nu_{\max}$ 2950, 1634 and 1029 cm⁻¹. ¹H-NMR δ_H 1.05 (24H, t *J* = 7.3 Hz, 8×CH₂CH₃), 1.45 (36H, s, 4×C(CH₃)₃), 2.95–3.15 (16H, m, 8×CH₂CH₃), 3.20–3.45 (4H, m, 2×CH₂N), 3.90–4.30 (4H, m, 2×CH₂N), 4.50 (8H, s, 4×CCH₂N), 7.10–7.50 (28H, m, 28×H_{Ar}), 8.00 (2H, s, 2×HC=N), 8.13 (2H, s, 2×HC=N). ¹³C-NMR δ_C 11.5, 30.0, 35.7, 46.91, 55.4, 57.3, 65.7, 119.2, 119.6, 126.3, 131.1, 132.5, 132.6, 134.4, 141.9, 164.9, 170.1.

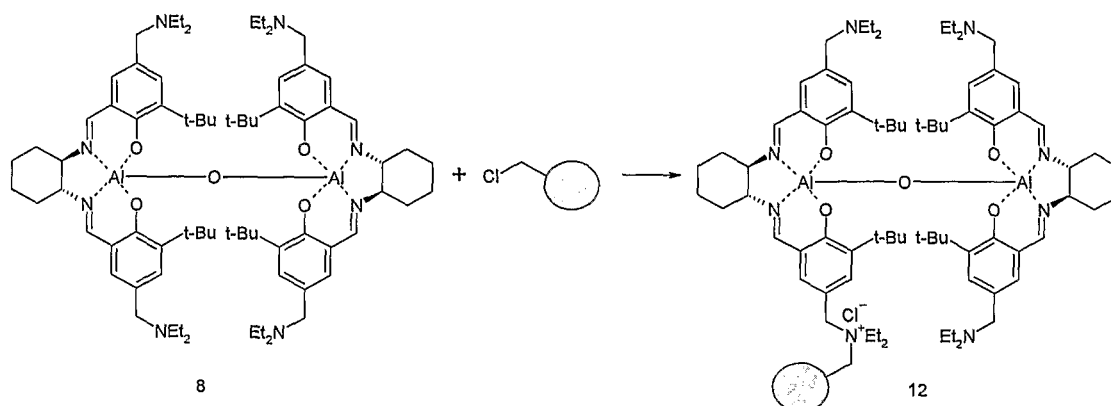


(e) Bis[(1*R*,2*R*)-*N,N'*-Bis(5-(*N*-benzyl-*N,N*-diethylaminomethyl)salicylidene bromide)cyclohexane-1,2-diaminoaluminium(III) oxide (25) and Bis[*N,N'*-Bis(5-(*N*-benzyl-*N,N*-diethylaminomethyl)salicylidene bromide)ethane-1,2-diaminoaluminium(III) oxide (26)]

Benzyl bromide (0.07 mL, 0.6 mmol) was added to a solution of bimetallic complex (23) or (24) (0.1 mmol) in propylene carbonate (10 mL) and the reaction stirred at 85°C for 16 hours. The solvent was evaporated *in vacuo* to give compound (25) or (26) as a pale orange powder.

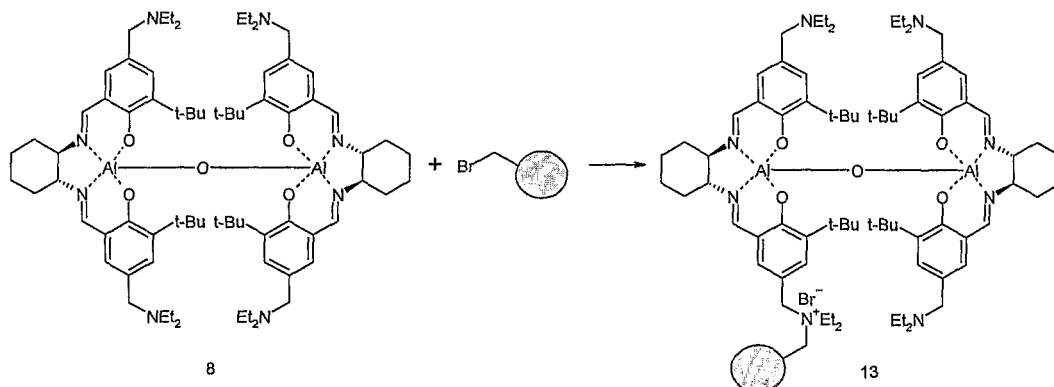
25: pale orange solid obtained in 52% yield. $[\alpha]^{20}_D -240$ (c 0.01, DMSO). ν_{max} 2923, 1625 and 1088 cm^{-1} . 1H -NMR δ_H (DMSO- d_6): 1.04-1.99 (24H, m, $8 \times CH_2CH_3$), 1.50-2.15 (16H, m, $2 \times (CH_2)_4$), 2.5-2.6 (16H, m, $8 \times CH_2CH_3$), 3.1-3.9 (12H, m, $4 \times CHN + 4 \times CCH_2N$), 4.50 (8H, s, $4 \times CCH_2N$), 6.74 (4H, d, $J = 7.3$ Hz, $4 \times H_{Ar}$), 6.82 (4H, d, $J = 7.3$ Hz, $4 \times H_{Ar}$), 7.13-7.46 (24H, m, $24 \times H_{Ar}$), 8.43 (4H, s, $4 \times HC=N$).

26: pale orange solid obtained in 40% yield. ν_{max} 2960, 1644 and 1032 cm^{-1} . 1H -NMR δ_H (DMSO- d_6): 0.99 (12H, m, $4 \times CH_3CH_2$), 1.52 (12H, m, $4 \times CH_3CH_2$), 3.21 (16H, q $J = 7.1$ Hz, $8 \times CH_2CH_3$), 4.1-4.3 (16H, m, $4 \times CCH_2N + 4 \times CH_2N$), 4.57 (8H, s, $4 \times CCH_2N$), 6.97 (4H, d, $J = 8.3$ Hz, $4 \times H_{Ar}$), 7.1-7.4 (24H, m, $24 \times H_{Ar}$), 7.5-7.6 (4H, m, $4 \times H_{Ar}$), 7.60 (4H, s, $4 \times HC=N$).

Example 2

- 5 Merrifield resin (120 mg, 0.2 mmol) was swollen in a minimal amount of DMF/dichloromethane. Complex (8) (240 mg, 0.4 mmol) was added and the mixture was stirred for 24 hours at 30°C. The resin was filtered off and washed using DMF (10 mL), DMF/dichloromethane (1:1) (10 mL), dichloromethane (10 mL), then it was dried under vacuum to give compound (12) as a yellow-coloured resin.

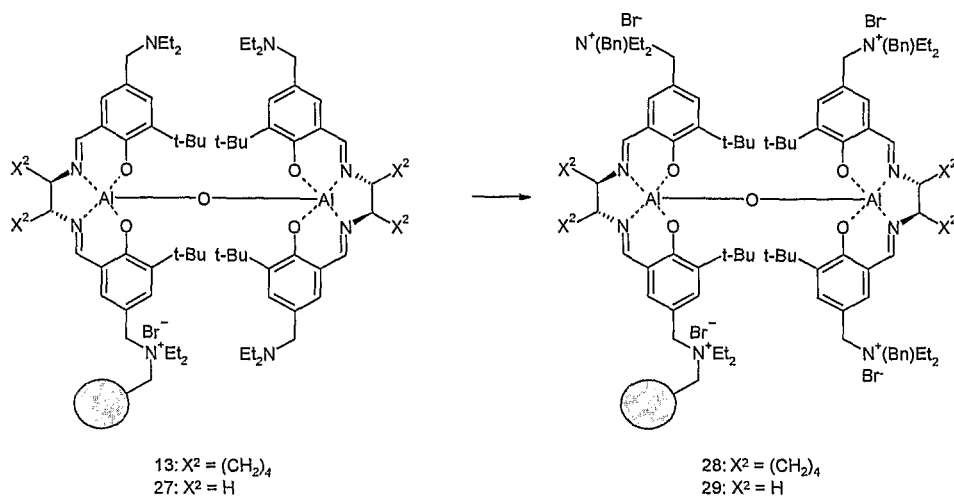
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Example 3

- (a) Merrifield resin (120 mg, 0.2 mmol) was converted into the corresponding bromomethyl resin by treatment with a large excess of tetrabutylammonium bromide for several days in dichloromethane / DMF. Complex (8) (240 mg, 0.4 mmol) was added to this resin and the mixture was stirred for 24 hours at 30°C. The resin was filtered off and was washed using DMF (10 mL), DMF/dichloromethane (1:1) (10 mL), dichloromethane (10 mL), then dried under vacuum to give yellow-coloured resin (13). $\nu_{\max}$ 2920, 2160, 1634, 1450 and 1066 cm^{-1} .

20

- (b) Immobilized catalyst 27 was synthesised from complex (22) in an analogous manner to step (a) above. 75% yield. $\nu_{\max}$ 2963, 2159, 1634, 1451 and 1091 cm^{-1} .

Example 4

A sample of resin (13) or (27) (0.04 mmol) was swollen in DMF/ CH_2Cl_2 and a large
 5 excess of benzyl bromide (40 mg, 0.24 mmol) was added. The mixture was stirred at
 room temperature for 24 hours, then the reaction was filtered and the resin washed
 with DMF (10 mL), DMF/ dichloromethane (1:1) (10 mL), dichloromethane (10 mL),
 then dried *in vacuo* to give a yellow-coloured resin.

(28): ν_{max} 2922, 2158, 1634, 1635, 1450 and 1028 cm^{-1}

10 (29): 83% yield. ν_{max} 2961, 2153, 1636, 1544 and 1023 cm^{-1}

Example 5

a) Complexes (10), (21), (25) and (26)

Complexes (10), (21), (25) and (26) were tested in the reaction of some terminal
 15 epoxides with carbon dioxide at room temperature and atmospheric pressure.

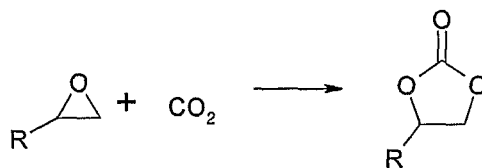


Table 1. Cyclic carbonate formation from epoxides.

Entry	Complex	R	TBAB (mol-%)	Time (h)	Conversion (%) ^a
1	10	Ph	0	3	71
2	10	Ph	0	6	97
3	10	Ph	2.5	3	74
4	10	<i>n</i> -Bu	0	3	30 ^b

5	10	<i>n</i> -Bu	0	6	63 ^b
6	10	<i>n</i> -Octyl	0	3	44
7	10	<i>n</i> -Octyl	0	6	81
8	10	CH ₂ OH	0	3	55
9	10	CH ₂ OH	0	6	79
10	10	CH ₂ Cl	0	3	59 ^b
11	10	CH ₂ Cl	0	6	81 ^b
12 ^c	10	Me	0	3	50 ^b
13 ^c	10	Me	0	6	62 ^b
14	21	Ph	0	3	69
15	21	Ph	0	6	88
16	21	Ph	0	24	99
17	25	Ph	0	3	48
18	25	Ph	0	6	60
19	25	Ph	0	24	73
20	26	Ph	0	3	54
21	26	Ph	0	6	69
22	26	Ph	0	24	89

Reactions carried out neat with dimeric Al(salen) complex (2.5 mol-%) and the corresponding epoxide (1 mmol) under carbon dioxide at 26 °C and 1 atm unless otherwise stated. ^a Determined by ¹H-NMR spectroscopy. ^b Volatile starting material was removed and the yield was determined by difference of weight. ^c Reaction

5 performed at 0 °C.

b) Complexes 12 & 13

These complexes were used at 2.5 mol% in propylene carbonate (5 eq.) and styrene oxide (1 mmol) under carbon dioxide at 26°C and 1 atmosphere pressure unless
 10 otherwise stated below. The reaction was carried out by dissolving the complexes (0.0415 mmol) in propylene carbonate (0.85g) in a sample vial fitted with a magnetic stirrer bar. Styrene oxide (200 mg, 1.66 mmol) was then added and the sample vial was placed in a large conical flask. The conical flask was placed in an oil bath thermostatted at 26°C. Cardice pellets were added to the conical flask which
 15 was fitted with a rubber stopper pierced by a deflated balloon. The reaction was stirred for the required length of time, then filtered to remove the supported catalyst which was washed thoroughly with CH₂Cl₂ (20 mL). The filtrate and washings were combined and evaporated *in vacuo* and the residue analysed by ¹H NMR

spectroscopy to determine the conversion of styrene oxide to styrene carbonate. The immobilized catalyst could be returned to the sample vial and reused, as shown with the repeated runs below.

Entry	Catalyst	Run	Time (h)	Conversion (%) ^a
1 ^{b,e}	12	1st	3	0
2 ^{b,c,d}	12	1st	3	17
3 ^{b,c,d}	12	2nd	3	9
4 ^c	12	1st	3	37
5 ^c	12	1st	6	67
6 ^c	12	1st	20	100
7 ^c	12	2nd	3	5
8 ^c	12	2nd	6	37
9 ^c	12	2nd	20	86
10 ^c	12	3rd	3	0
11 ^c	12	3rd	6	20
12 ^c	12	3rd	20	63
13	13	1st	3	11
14	13	1st	6	69
15	13	1st	20	100
16	13	2nd	3	0
17	13	2nd	6	37
18	13	2nd	20	94
19	13	3rd	3	5
20	13	3rd	6	25
21	13	3rd	20	70

- 5 ^a Determined by GC. ^b Reaction performed solvent-free. ^c Reaction performed in the presence of 2.5 mol% of TBAB. ^d Only 0.5 mol% of the complex (12) was used.

The use of propylene carbonate as a solvent is compatible with the catalytic system.

10 *c) Complexes (28) and (29)*

Complexes (28) and (29) were tested at 2.5 mol% in the in the reaction of styrene oxide (1 mmol) with carbon dioxide at 26°C and 1 atmosphere pressure in the presence of propylene carbonate (5 eq.) as a solvent, with 20 hours for each

reaction. The complexes were found to be recyclable. The method is as in step b) above.

Complex (28) gave styrene carbonate yields of 79, 73, 66 and 60% over four consecutive reactions.

Complex (29) gave styrene carbonate yields of 79, 71, 67 and 64% over four consecutive reactions.

10 Example 6

(a) Synthesis of $[\text{Al}(\text{salen})]_2\text{O}$ electrostatically supported on clays.

Clays (0.5 g) were activated at 120°C for three days prior to use. After the activation, the clay (0.5 g) was added to a solution of aluminium complex (21) (0.140 g, 0.08 mmol) in DMF (30 mL) and refluxed for 30 hours. Subsequently, the mixture was filtered and washed with DMF (4x20 mL), EtOAc (4x20 mL) and dichloromethane (3x20 mL) to yield a powder which was dried under vacuum for 24 hours.

$[\text{Al}(\text{salen})]_2\text{O}$ supported on Bentonite (30): Pale brown solid, yield 99%. ν_{max} 3540, 2150, 1987 and 1659 cm^{-1} .

20

$[\text{Al}(\text{salen})]_2\text{O}$ supported on Montmorillonite K10 (31): Purple solid, yield 99%. ν_{max} 3500, 1659 and 922 cm^{-1} .

$[\text{Al}(\text{salen})]_2\text{O}$ supported on Al pillared clay (32): Pale brown solid, yield 99%. ν_{max} 3500, 1654 and 1034 cm^{-1} .

25

(b) Synthesis of styrene carbonate using $[\text{Al}(\text{salen})]_2\text{O}$ electrostatically supported on clays

Styrene oxide (0.2 g, 1.66 mmol) and catalyst (30-32) (0.5 g, 0.1 mmol/g support) in propylene carbonate (0.84 g) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. The conical flask was placed in an oil bath thermostatted at 26°C. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The contents of the reaction vial were stirred for 24 hours during which time the balloon inflated as the cardice pellets evaporated. The reaction was filtered to remove supported catalyst

35

and the solution analysed by GC to determine the conversion of styrene oxide into styrene carbonate.

Catalyst Conversion(%)

30	5%	5
31	3%	
32	7%	

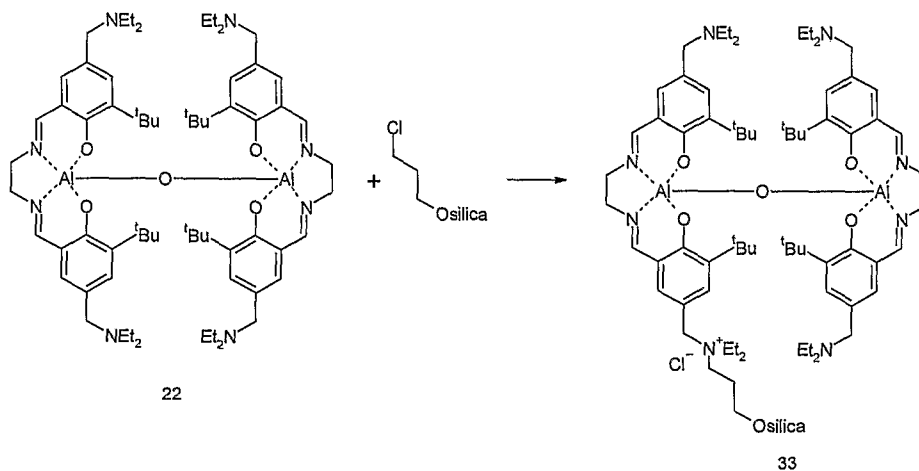
Example 7

10 **(a) Synthesis of modified SiO₂**

(3-Chloropropyl)-triethoxysilane (0.16 mL, 2 mmol) was added to a mixture of activated SiO₂ (2g) in dry toluene (25 mL) and refluxed under N₂ for 24 hours. Subsequently, the mixture was filtered and washed with EtOAc (4x50 mL) to yield a yellow powder (95%). $\nu_{\max}$ 2505, 2160 and 1975 cm⁻¹.

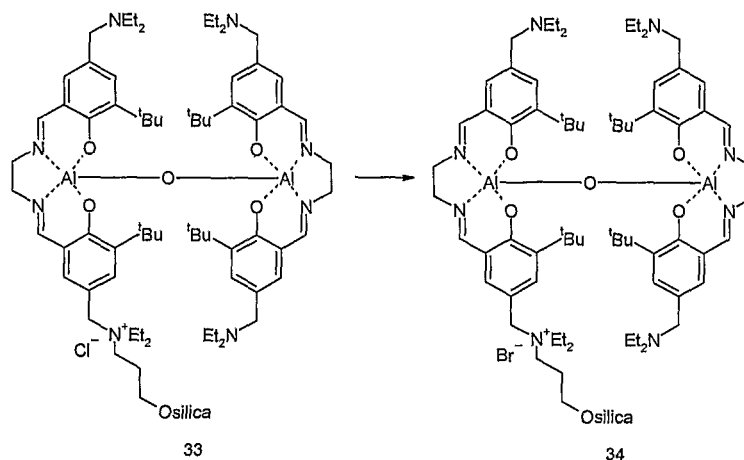
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(b) Synthesis of [Al(salen)]₂O⁺Cl⁻ supported on modified SiO₂ (33)

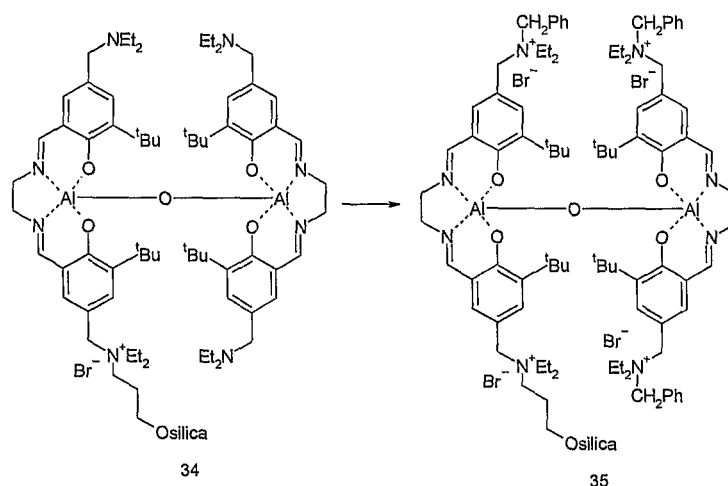


Modified SiO₂ (0.1 g) was added to a solution of aluminium complex (22) (0.175 g, 0.15 mmol) in CH₃CN (40 mL) and the mixture was refluxed overnight. Then, the mixture was filtered and washed with EtOAc (4x50 mL) to give silica supported complex (33) as a yellow powder. $\nu_{\max}$ 3500, 1649 and 1070 cm⁻¹.

20

(c) Synthesis of $[\text{Al}(\text{salen})]_2\text{O}^+\text{Br}^-$ supported on modified SiO_2 (34)

Tetrabutylammonium bromide (193 mg, 6 mmol) was added to a suspension of supported complex (33) (0.220 g, 1 mmol) in CH_3CN (40 mL) and the resulting mixture was refluxed overnight. Then, the mixture was filtered and washed with EtOAc (4x50 mL) to give silica supported complex (34) as a yellow powder. ν_{max} 3427, 1628 and 1070 cm^{-1} .

(d) Synthesis of benzylated $[\text{Al}(\text{salen})]_2\text{O}^+\text{Br}^-$ supported on modified SiO_2 (35)

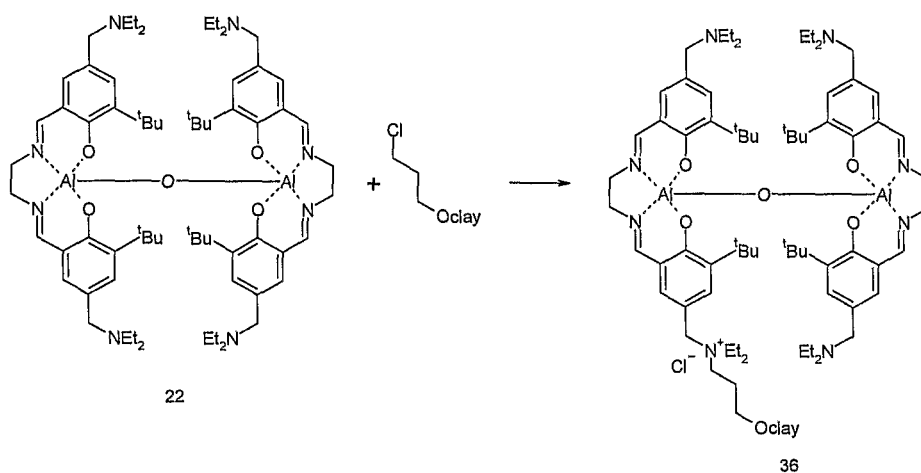
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Benzyl bromide (0.09 mL, 0.72 mmol) was added to a suspension of supported catalyst (34) (0.240 g, 1 mmol) in CH_3CN (40 mL) and the resulting mixture was refluxed overnight. Subsequently, the mixture was filtered and washed with EtOAc (4 x 50 mL) to give silica supported complex (35) as a yellow powder. ν_{max} 3410, 1633 and 1078 cm^{-1} .

15

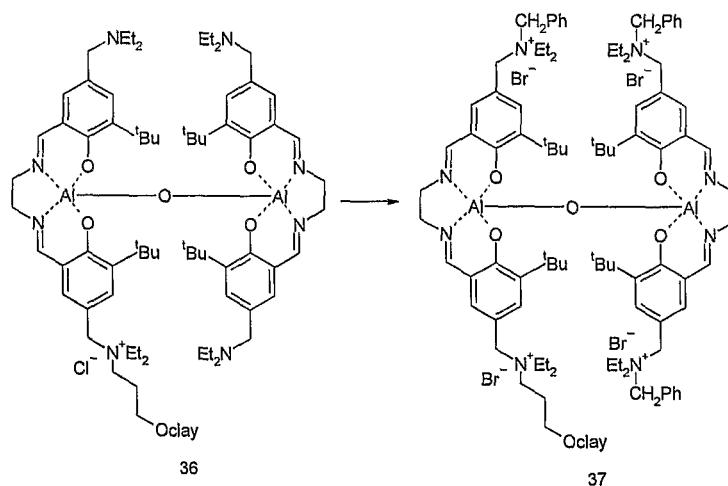
Example 8**(a) Synthesis of modified Al pillared clay**

(3-Chloropropyl)-triethoxysilane (0.16 mL, 2 mmol) was added to a mixture of activated Al pillared clay (2 g) in dry toluene (25 mL) and the mixture was refluxed under N₂ for 24 hours. Then, the mixture was filtered and washed with EtOAc (4x50 mL) to give a yellow powder (95%). $\nu_{\max}$ 3512 and 1028 cm⁻¹.

(b) Synthesis of [Al(salen)]₂O⁺Cl⁻ supported on modified Al pillared clay (36)

Modified Al pillared clay (0.1 g) was added to a solution of aluminium complex (22) (0.175 g, 0.15 mmol) in CH₃CN (40 mL) and the mixture was then refluxed overnight. Subsequently, the mixture was filtered and washed with EtOAc (4x50 mL) and dichloromethane (3x 50 mL) to give clay supported complex (36) as a yellow powder. $\nu_{\max}$ 3410, 1627 and 1031 cm⁻¹.

15

(c) Synthesis of benzylated [Al(salen)]₂O⁺Br⁻ supported on modified Al pillared clay (37)

Benzyl bromide (0.09 mL, 0.72 mmol) and tetrabutylammonium bromide (193 mg, 6 mmol) were added to a solution of supported complex (36) (0.220 g, 1 mmol) in CH₃CN (40 mL) and the resulting mixture was refluxed overnight. Subsequently, the mixture was filtered and washed with EtOAc (4x50 mL) to give clay supported complex (37) as a yellow powder. $\nu_{\max}$ 3415, 1627 and 1028 cm⁻¹.

Example 9: Synthesis of styrene carbonate using supported catalysts (35) and (37)

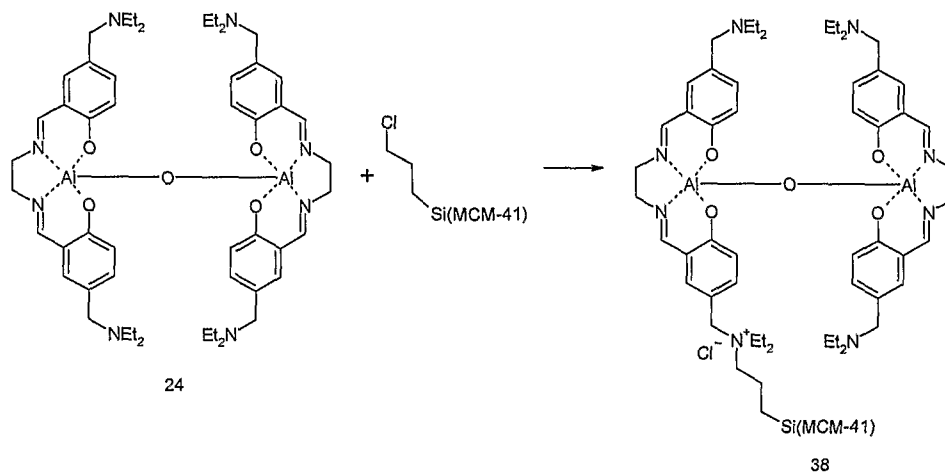
Styrene oxide (0.2 g, 1.66 mmol) and catalyst (35) or (37) (0.083 g, 0.5 mmol/g support) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. The conical flask was placed in an oil bath thermostatted at 26°C. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The contents of the reaction vial were stirred for 24 hours during which time the balloon inflated as the cardice pellets evaporated. The reaction was filtered to remove supported catalyst and the solution analysed by GC to determine the conversion of styrene oxide into styrene carbonate.

Catalyst	Conversion (%)
35	86
37	21

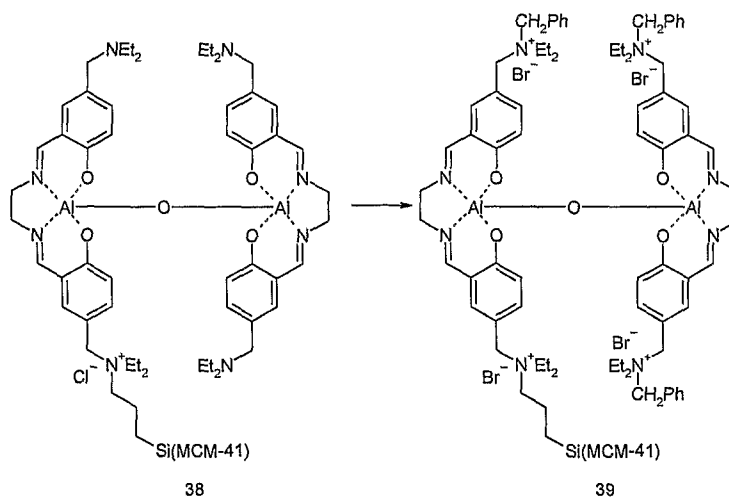
Example 10

(a) Synthesis of modified MCM-41

(3-Chloropropyl)-triethoxysilane (0.16 mL, 2 mmol), was added to a suspension of activated MCM-41 (2 g) in dry toluene (25 mL) and the mixture refluxed under N₂ for 24 hours. The mixture was then filtered and washed with EtOAc (4 x 50 mL) to give a white powder (94%). $\nu_{\max}$ 2681, 1711, 1057 and 807 cm⁻¹.

(b) Synthesis of $[\text{Al}(\text{salen})]_2\text{O}^+\text{Cl}^-$ supported on modified MCM-41 (38)

3-Chloropropyl modified MCM-41 (0.52 g) was added to a solution of aluminium
 5 complex (22) (1.50 g, 0.45 mmol) in CH_3CN (40 mL) and the mixture refluxed
 overnight. Then, the reaction was filtered and washed with EtOAc (6 x 50 mL) to
 leave MCM-41 supported complex (38) as a yellow powder (0.86 g, 86%). ν_{max} 3122,
 1628, 1057 and 789 cm^{-1} .

(c) Synthesis of benzylated $[\text{Al}(\text{salen})]_2\text{O}^+\text{Br}^-$ supported on modified MCM-41 (39)

Tetrabutylammonium bromide (0.20 g, 0.6 mmol) and benzyl bromide (0.13 g, 1
 mmol) were added to a suspension of supported aluminium complex (38) (200 mg,
 15 0.15 mmol) in CH_3CN (30 mL) and the mixture was refluxed overnight. Then, the
 mixture was washed with EtOAc (4 x 50 mL) to leave MCM-41 supported complex
 (39) as a yellow powder (0.22 g, 98%). ν_{max} 3452, 1634, 1052 and 947 cm^{-1} . ICPMS
 (5 mg of supported catalyst digested with 5 mL of 1M HCl) gave an aluminium

concentration of 22.55 ppm, corresponding to a catalyst loading of 0.47 mmol per gram of support.

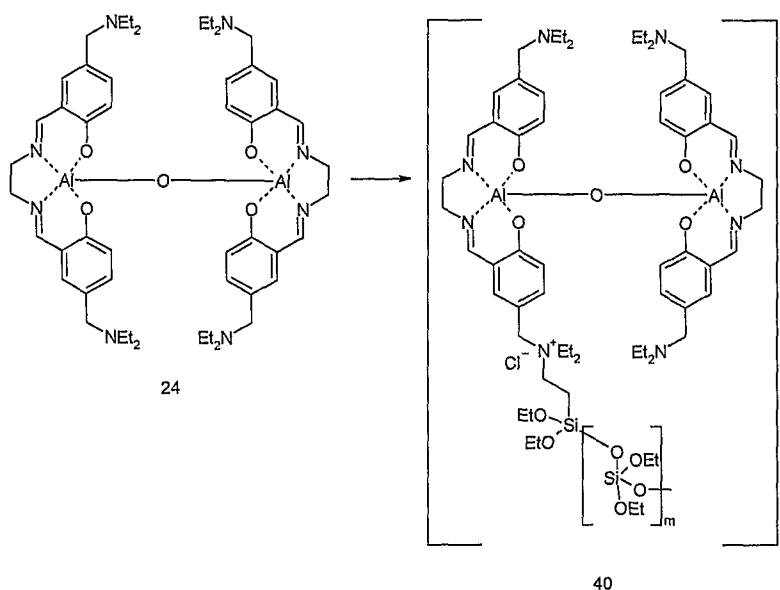
Example 11: Synthesis of styrene carbonate using supported catalyst (39)

- 5 Styrene oxide (1.66 mmol), catalyst (39) (0.0415 mmol) and propylene carbonate (0.845 g) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. The conical flask was placed in an oil bath thermostatted at 26°C. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The reaction was stirred for 24 hours with
10 samples being removed after 3, 6 and 24 hours for analysis by GC/MS to determine the conversion of epoxide to cyclic carbonate. The results were:

<u>Time (hours)</u>	<u>Conversion (%)</u>
3	12
6	23
24	57

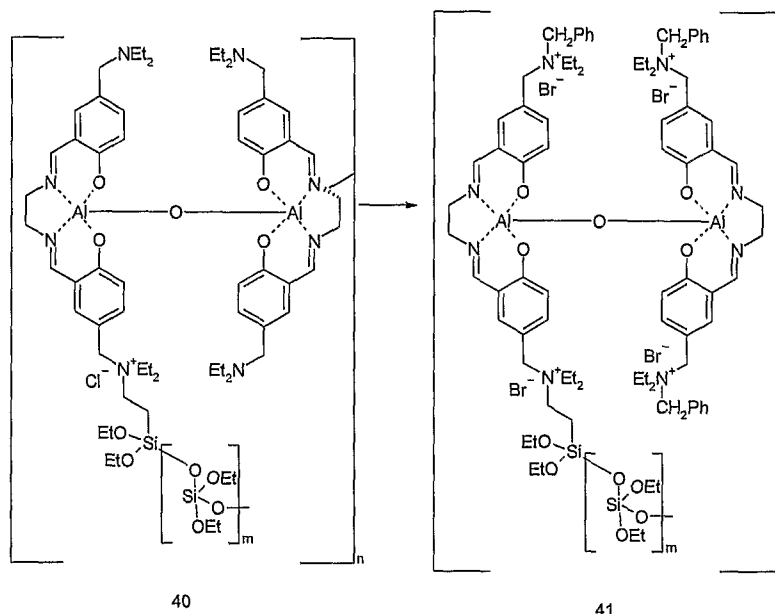
Example 12: Synthesis of ethylene carbonate using supported catalyst (39)

- 15 Catalyst (39) (0.0503 mmol) and propylene carbonate (1.0g) were added to a reaction vial to which pre-cooled ethylene oxide (2.01 mmol) was added. The reaction vial was fitted with a magnetic stirrer and placed inside a stainless steel reaction vessel along with sufficient cardice pellets to pressurise the system to approximately 6 atmospheres. The stainless steel reactor was sealed and the
20 reaction left to stir for 24 hours after which the reaction mixture was taken up in ethyl acetate and filtered to remove the catalyst. The ethyl acetate was evaporated under reduced pressure and the weight of the residue determined. The relative composition of propylene and ethylene carbonates was determined by GC/MS and used to calculate that a 93% conversion of ethylene oxide to ethylene carbonate had been
25 achieved.

Example 13**(a) Synthesis of $[\text{Al}(\text{salen})]_2\text{O}^+\text{Cl}^-$ supported on solgel (40)**

m is approximately 10

- 5 (3-Chloropropyl)-triethoxysilane (0.12 g, 0.5 mmol) was added to a solution of aluminium complex (22) (0.55 g, 0.5 mmol) in CH_3CN (40 mL) and the reaction was refluxed overnight. Then the solvent was removed to leave a product which was dissolved in EtOH (2 mL). $\text{Si}(\text{OEt})_4$ (1.12 mL, 5 mmol) was added to this solution and the mixture stirred for 2 minutes at room temperature. Then, H_2O (3 mL) and NH_4OH
- 10 (3 drops) were added and the mixture was vigorously stirred for 5 min. The mixture was left undisturbed for 5 days and then placed in an oven at 110°C for further two days. The resulting solid was washed with isopropanol (2 x 25 mL) and CH_3CN (2 x 25 mL) and dried overnight at 110°C to leave the solgel supported catalyst (40) (0.42 g, 41%). ν_{max} 2914, 1633 and 1067 cm^{-1} .

(b) Synthesis of benzylated $[Al(salen)]_2O^+Br^-$ supported on solgel (41)

m is approximately 10

Tetrabutylammonium bromide (0.20 g, 0.6 mmol) and benzylbromide (0.13 g, 1 mmol) were added to a suspension of supported aluminium complex (40) in CH_3CN (30 mL) and the mixture refluxed overnight. Then, the mixture was washed with EtOAc (4 x 50 mL) to leave solgel supported catalyst (41) as a yellow powder (0.52 g, 96%). ν_{max} 3562, 1629 and 1052 cm^{-1} . ICPMS (5 mg of supported catalyst digested with 10 mL of 1M HCl) gave an aluminium concentration of 13.65 ppm, corresponding to a catalyst loading of 0.51 mmol per gram of support.

Example 14: Synthesis of styrene carbonate using supported catalyst (41)

Styrene oxide (1.66 mmol), catalyst (41) (0.0415 mmol) and propylene carbonate (0.845 g) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. The conical flask was placed in an oil bath thermostatted at 26°C. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The reaction was stirred for 24 hours with samples being removed after 3, 6 and 24 hours for analysis by GC/MS spectroscopy to determine the conversion of epoxide to cyclic carbonate. The results were:

<u>Time (hours)</u>	<u>Conversion (%)</u>
3	10
6	20
24	52

Example 15: Synthesis of ethylene carbonate using supported catalysts (29), (35) and (41)

- (a) Catalyst (41) (0.0503 mmol) and propylene carbonate (1.0g) were added to a reaction vial to which pre-cooled ethylene oxide (2.01 mmol) was added. The reaction vial was fitted with a magnetic stirrer and placed inside a stainless steel reaction vessel along with sufficient cardice pellets to pressurise the system to approximately 6 atmospheres. The stainless steel reactor was sealed and the reaction left to stir for 24 hours after which the reaction mixture was taken up in ethyl acetate and filtered to remove the catalyst. The ethyl acetate was evaporated *in vacuo* and the weight of the residue determined. The relative composition of propylene and ethylene carbonates was determined by GC/MS and used to calculate that a 97% conversion of ethylene oxide to ethylene carbonate had been achieved.
- (b) The above procedure was used but with catalyst (29) and resulted in 95% conversion of ethylene oxide to ethylene carbonate after a reaction time of 24 hours.
- (c) The above procedure was used but with catalyst (35) and resulted in 81% conversion of ethylene oxide to ethylene carbonate after a reaction time of 24 hours.

Example 16: Use of immobilised catalysts to convert ethylene oxide into ethylene carbonate under continuous flow conditions

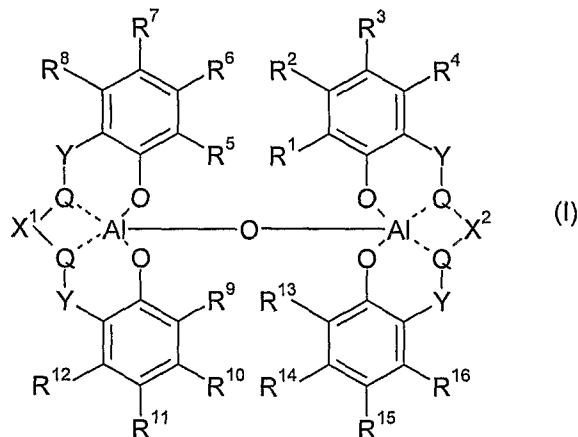
The flow reactor is illustrated in Figure 1. Ethylene oxide was collected from a commercially supplied cylinder as a liquid in a cooled beaker at -78°C and placed, with a magnetic stirrer bar, inside a 360 mL pre-cooled (-10 to -40°C) stainless steel pressure vessel (3). The vessel was then sealed. Nitrogen and carbon dioxide gases were supplied from cylinders via mass flow controller units (1) and their respective lines merged to the inlet of the pressure vessel (see diagram). All tubing used in the system was composed of stainless steel with an internal diameter of approximately 1.6mm. The temperature of the pressure vessel (3) was controlled by a cryostatically cooled bath (2) to provide the required rate of evaporation of ethylene oxide at a particular flow rate of N₂ and CO₂. This was determined by passing the vessel outlet line directly into a GC system (6) fitted with a column capable of separating the three gases. The vessel outlet line was then connected to a stainless steel tubular reactor (4) (15 cm x 10 mm) packed with a solid supported catalyst and plugged at both ends with a small volume of cotton. The tubular reactor (4) was either kept at ambient temperature or immersed in a thermostatted water bath. The mixture of CO₂,

- ethylene oxide and N₂ was passed through the reactor column at a steady flow rate. The outlet of the reactor (4) was connected to a sealed glass vial (5) via a needle to collect any non-gaseous products. The outlet from the product receptacle passed to a GC system (6) which was used to determine the concentrations of CO₂, N₂ and
- 5 ethylene oxide in the effluent gas stream. The results obtained with both silica and polystyrene supported catalysts are given in the following table.

Run	Catalyst (amount g)	N ₂ flow (mL/min)	CO ₂ flow (mL/min)	Pressure vessel temperature (°C)	Ethylene oxide consumption (mL/h)	Time (h)	Reactor temperature (°C)	Ethylene carbonate yield
1	29 (2.51)	25	25	-40	1.0	19	ambient	0.14 g, 0.15%
2	35 (1.95)	25	25	-40	1.0	19	ambient	0.08 g, 0.1%
3	35 (1.17)	2.5	2.5	-10	0.21	120	ambient	1.1 g, 1.5%
4	35 (1.17)	2.5	1.0	-10	0.15	96	ambient	1.5 g, 4%
5	35 (3.52)	2.5	1.0	-10	0.15	46	ambient	2.4 g, 21%
6	35 (3.52)	2.5	1.0	-10	0.15	25	50	3.4 g, 53%
7	35 (3.52)	2.5	1.0	-10	0.15	7	60	1.49 g, 80%

CLAIMS

1. A dimeric aluminium(salen) catalyst of formula I:



5 wherein:

Y-Q is $\text{CR}^{\text{C1}}=\text{N}$ or $\text{CR}^{\text{C1}}\text{R}^{\text{C2}}-\text{NR}^{\text{N1}}$, where R^{C1} , R^{C2} and R^{N1} are independently selected from H, halo, optionally substituted C_{1-20} alkyl, optionally substituted C_{5-20} aryl, ether and nitro;

each of the substituents R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} ,
 10 and R^{16} , is independently selected from H, halo, optionally substituted C_{1-20} alkyl, optionally substituted C_{5-20} aryl, optionally substituted C_{3-20} heterocyclyl, ether and nitro;

X^1 and X^2 are independently either (i) a C_{2-5} alkylene chain, which is optionally substituted by one or more groups selected from C_{1-4} alkyl and C_{5-7} aryl, or a C_{1-3} bisoxyalkylene chain, which is optionally substituted by one or more groups selected
 15 from C_{1-4} alkyl and C_{5-7} aryl or (ii) represent a divalent group selected from C_{5-7} arylene, C_{5-7} cyclic alkylene and C_{3-7} heterocyclylene, which may be optionally substituted;

(i) (a) at least one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} ,
 20 and R^{16} is selected from L-A, where L is a single bond or a C_{1-10} alkylene group and A is an ammonium group paired with a counterion selected from Cl, Br and I; and/or

(b) at least one of X^1 and X^2 is a divalent C_{3-7} heterocyclene group, containing a ring atom which is a quaternary nitrogen atom paired with a counterion
 25 selected from Cl, Br and I; and/or

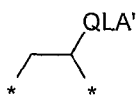
(c) at least one of X^1 and X^2 is a C_{2-5} alkylene chain or a C_{1-3} bisoxyalkylene chain, substituted by a group -Q-L-A, where Q is either $-\text{C}(=\text{O})-\text{O}-$, $-\text{C}(=\text{O})-\text{NH}-$, or a single bond;

and/or

- (ii) (a) one of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}$, and R^{16} is $L-A'$, where L is as defined above and A' is an ammonium linking group bound to a solid support and paired with a counterion selected from Cl, Br and I ; or
- 5 (b) one of X^1 and X^2 is a divalent C_{3-7} heterocyclene group, containing a ring atom which is a quaternary nitrogen forming part of an ammonium linking group bound to a solid support and paired with a counterion selected from Cl, Br and I ; or
- 10 (c) one of X^1 and X^2 is a C_{2-5} alkylene chain or a C_{1-3} bisoxyalkylene chain, substituted by a group $-Q-L-A'$.
2. A catalyst according to claim 1, wherein $Y-Q$ is $CR^{C1}=N$.
3. A catalyst according to claim 2, wherein R^{C1} is selected from H and C_{1-4} alkyl.
- 15 4. A catalyst according to claim 1, wherein $Y-Q$ is $CR^{C1}R^{C2}-NR^{N1}$, and R^{C1}, R^{C2} and R^{N1} are H .
5. A catalyst according to any one of the preceding claims, wherein $R^4 = R^8 =$
- 20 $R^{12} = R^{16} = H$.
6. A catalyst according to any one of the preceding claims, wherein those of $R^1, R^2, R^3, R^5, R^6, R^7, R^9, R^{10}, R^{11}, R^{13}, R^{14}, R^{15}$ and R^{16} which do not comprise $-L-A$ or $L-A'$ are independently selected from H, C_{1-7} alkyl, ether and nitro.
- 25 7. A catalyst according to any one of the preceding claims, wherein L is an unsubstituted C_{1-3} alkylene group.
8. A catalyst according to any one of the preceding claims where (a) at least one
- 30 of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}$, and R^{16} is selected from $L-A$; and/or (b) at least one of X^1 and X^2 is a divalent C_{3-7} heterocyclene group, containing a ring atom which is a quaternary nitrogen atom paired with a counterion selected from Cl, Br and I ; and/or (c) at least one of X^1 and X^2 is a C_{2-5} alkylene chain or a C_{1-3} bisoxyalkylene chain, substituted by a group $-Q-L-A$, where Q is either -
- 35 $C(=O)-$ or a single bond, is immobilized on a solid support, either by the use of steric effects or by electrostatic binding.

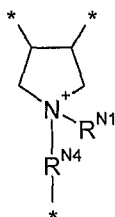
9. A catalyst according to any one of claims 1 to 8, wherein one of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , and R^{16} is selected from L-A' and A' is selected from $-\text{NH}(\text{CH}_3)(\text{CH}_2)-$, $-\text{NH}(\text{CH}(\text{CH}_3)_2)(\text{C}(\text{CH}_3)_2)-$, $-\text{N}(\text{CH}_3)_2(\text{CH}_2)-$,
 5 $-\text{N}(\text{CH}_2\text{CH}_3)_2(\text{CH}_2\text{CH}_2)-$, and $-\text{NHPh}(\text{CH}_2)-$.

10. A catalyst according to any one of claims 1 to 8, wherein X^1 or X^2 is substituted by -Q-L-A' and is of formula:



10

11. A catalyst according to any one of claims 1 to 8, wherein X^1 or X^2 is a divalent C_{3-7} heterocyclene group containing a ring atom which is a quaternary nitrogen forming part of an ammonium linking group, and is of formula:



- , where R^{N1} is selected from H, C_{1-7} alkyl and C_{5-20} aryl and where R^{N4} is a
 15 C_{1-7} alkylene group.

12. A catalyst according to any one of claims 1 to 9, wherein X^1 and X^2 are independently selected from is $-(\text{CH}_2)_n-$ or $-\text{O}-(\text{CH}_2)_p-\text{O}-$, and n is 2 or 3 and p is 1 or
 20 2.

13. A catalyst according to claim 12, wherein X^1 and X^2 are both $-\text{C}_2\text{H}_4-$.

14. A catalyst according to any one of claims 1 to 9, wherein X^1 and X^2 independently represent C_6 cyclic alkylene or benzylene.

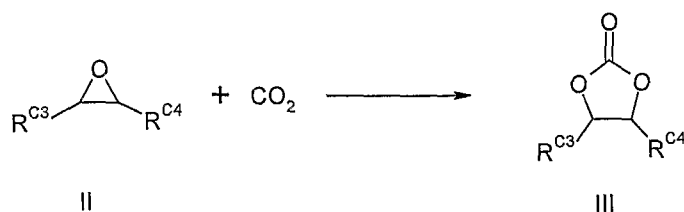
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15. A catalyst according to any one of claims 1 to 9, wherein X^1 and X^2 independently represent a divalent group selected from C_{5-7} arylene, C_{5-7} cyclic alkylene and C_{3-7} heterocyclene and is unsubstituted.

16. A catalyst according to any one of claims 1 to 15, wherein the ammonium counter group is Br.

17. A process for the production of cyclic carbonates comprising contacting an epoxide with carbon dioxide in the presence of a dimeric aluminium(salen) catalyst according to any one of claims 1 to 15.

18. The process of claim 17, wherein the catalysed reaction is:



wherein R^{C3} and R^{C4} are independently selected from H, optionally substituted C₁₋₁₀ alkyl, optionally substituted C₃₋₂₀ heterocyclyl and optionally substituted C₅₋₂₀ aryl, or R^{C3} and R^{C4} form an optionally substituted linking group between the two carbon atoms to which they are respectively attached.

19. The process according to claim 18, wherein R^{C4} is H.

20. The process according to either claim 18 or claim 19, wherein R^{C3} is selected from optionally substituted C₁₋₄ alkyl and optionally substituted C₅₋₇ aryl.

21. The use of a dimeric aluminium(salen) catalyst according to any one of claims 1 to 16 for the production of cyclic carbonates from epoxides.