SYNTHESIS OF CYCLIC CARBONATES

The present invention relates to aluminium(acen) and aluminium (salacen) complexes and their use as catalysts for synthesising cyclic carbonates from epoxides and carbon dioxide.

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; Zevenhoven *et al. Cat. Today* **2006**, *115*, 73-79).

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 $(n\text{Butyl})_4NI$ 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.

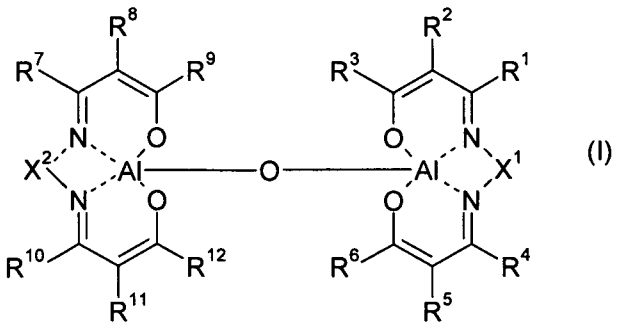
Metal(salen) complexes, including aluminium(salen) complexes, are well-known in the art for their use as catalysts. Lu, *et al.*, *App. Cat. A,* **234** (2002), 25-33, describes the use of a monomeric aluminium(salen) catalyst.

Also known in the art is the method of synthesising aluminium(salen) catalysts by treating a salen ligand with Me_3Al, Et_3Al, Me_2AlCl, Me_2AlOTf, Et_2AlBr or Et_2AlCl in a 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 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 WO 2008/132474. In copending application PCT/GB2009/000624, the present inventor has also discovered that the cocatalyst can be combined into the catalyst molecule, and that the combined catalysts and co-catalyst can be immobilised on a solid support.

The present inventor has now found that it is possible to simplify the structure of the catalyst. The catalysts disclosed below have cheaper starting materials (e.g. acetylacetone), and the starting materials are more readily available.

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

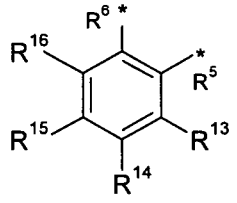


(I)

wherein:

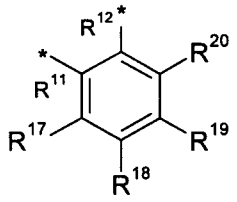
a) each of the substituents R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12}, is independently selected from H, halo, optionally substituted C_{1-20} alkyl (including CAr_3, where Ar is a C_{5-20} aryl group), optionally substituted C_{5-20} aryl, optionally substituted C_{3-20} heterocyclyl, ether and nitro, where R^2, R^5, R^8 and R^{11} may additionally be independently selected from optionally substituted ester or optionally substituted acyl or the pairs of R^2 and R^3, R^5 and R^6, R^8 and R^9 and R^{11} and R^{12} may independently together form a C_{2-4} alkylene chain, optionally substituted by one or more groups selected from C_{1-4} alkyl and C_{5-7} aryl; or

b) R^5 and R^6 together with the carbon atoms to which they are attached form an optionally substituted benzene ring of formula:



, and

R^{11} and R^{12} together with the carbon atoms to which they are attached form an optionally substituted benzene ring of formula:



,

each of the substituents R^1, R^2, R^3, R^4, R^7, R^8, R^9, R^{10}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20}, 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_{9-10} arylene, bi-C_{5-7} aryl, bi-C_{9-10} aryl, C_{5-7} cyclic alkylene and C_{3-7} heterocyclylene, which may be optionally substituted.

In a second aspect, the present invention provides a catalyst defined in the first aspect of the invention, except that:

(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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) is selected from L-A, where L is a single bond or a C_{1-10} alkylene group and A is an onium 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 forming part of an ammonium group 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)-O-, -C(=O)-NH-, or a single bond; and/or

(d) at least one of R^2, R^5, R^8 and R^{11} is -Q'-L-A, where Q' is either -C(=O)-O- or -C(=O)-;

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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) is L-A', where L is as defined above and A' is an onium 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'; or

(d) one of R^2, R^5, R^8 and R^{11} is -Q'-L-A'.

Thus, in catalysts of the second aspect, 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.

The catalysts of the first aspect or the second aspect 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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) 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 forming part of an ammonium group; 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)-O-, -C(=O)-, NH or a single bond and/or (d) at least one of R^2, R^5, R^8 and R^{11} is -Q'-L-A, where Q' is either -C(=O)-O- or -C(=O)-, may be immobilized on a solid support, either by the use of steric effects or by electrostatic binding.

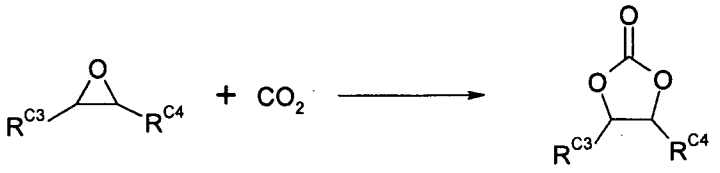
If the catalyst of the first or second aspects includes one or more chiral centres, then it may be a (wholly or partially) racemic mixture or other mixture thereof, for example, a mixture enriched in one enantiomer or diastereoisomer, a single enantiomer or diastereoisomer, or a mixture of the stereoisomers. 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 readily obtained by adapting the methods taught herein, or known methods, in a known manner. Preferably the catalyst of the first and second aspects is a single enantiomer, if a chiral centre is present.

In some embodiments, it is preferred that the catalysts are symmetrical, i.e. that the two aluminium ligands are the same. Therefore, it may be preferred that $X^1=X^2$, $R^1=R^7$, $R^2=R^8$, $R^3=R^9$, $R^4=R^{10}$, $R^5=R^{11}$, $R^6=R^{12}$ and (if present) $R^{13}=R^{17}$, $R^{14}=R^{18}$, $R^{15}=R^{19}$ and $R^{16}=R^{20}$.

A third 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(acen) or aluminium(salacen) catalyst according to the first aspect of the invention in combination with a co-catalyst capable of supplying Y^-, where Y is selected from Cl, Br and I; or in the presence of a dimeric aluminium(acen) or aluminium(salacen) catalyst according to the second aspect of the invention.

The cocatalyst is preferably soluble in the reaction mixture. Suitable sources of Y^- are MY, 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.

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



III IV

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 C_{1-10} alkyl, optionally substituted C_{3-20} heterocyclyl and optionally substituted C_{5-20} aryl.

A possible substituent for the C_{1-10} alkyl group is a C_{5-20} aryl group.

The third aspect of the invention also provides the use of a dimeric aluminium(acen) or aluminium (salacen)) catalyst of the first aspect of the invention in combination with a co-catalyst capable of supplying Y^-, or a dimeric aluminium(acen) or aluminium(salacen) catalyst of the second aspect of the invention for the production of cyclic carbonates from epoxides.

A fourth aspect of the invention provides a process for the synthesis of a dimeric aluminium(acen) or aluminium(salacen) catalyst of formula I according to the first or second aspects of the invention.

Detailed description of the invention

Definitions

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



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} heterocylyl group. The C_{5-20} cycloalkyl or C_{5-20} heterocylyl group may be substituted only in a single position on the ring, for example, adjacent the epoxide. Suitable substituents, include optionally substituted C_{1-10} alkyl, optionally substituted C_{3-20} heterocyclyl and optionally substituted C_{5-20} aryl.

The optional substituents may be selected from: C_{1-10} alkyl, C_{3-20} heterocyclyl, C_{5-20} aryl, halo, hydroxy, ether, cyano, nitro, carboxy, ester, amido, amino, acylamido, ureido, acyloxy, thiol, thioether, sulfoxide, sulfonyl, thioamido and sulfonamino.

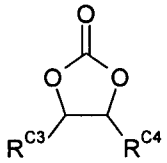
In some embodiments, the C_{1-10} alkyl group is substituted by a C_{5-20} aryl group.

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 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).

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.

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

(a) covalent binding (those where 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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (if present) is selected from L-A' or one of X^1 and X^2 contains a quaternary nitrogen forming part of an ammonium linking group);

(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 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 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-chloropropyloxy group by treatment with (3-chloropropyl)triethoxysilane. Another example is Al pillared clay, which can also be modified to include a 3-chloropropyloxy 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-chloropropyl 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-aluminium 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. C_{1-4}, C_{1-7}, C_{1-20}, C_{2-7}, C_{3-7}, etc.) denote the number of carbon atoms, or the range of number of carbon atoms. For example, the term "C_{1-4} alkyl", as used herein, pertains to an alkyl group having from 1 to 4 carbon atoms. Examples of groups of alkyl groups include C_{1-4} alkyl ("lower alkyl"), C_{1-7} alkyl and C_{1-20} 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 "C_{1-7} alkylene", as used herein, pertains to an alkylene group having from 1 to 7 carbon atoms.

Examples of (unsubstituted) saturated alkyl groups include, but are not limited to, methyl (C_1), ethyl (C_2), propyl (C_3), butyl (C_4), pentyl (C_5), hexyl (C_6), and heptyl (C_7).

Examples of (unsubstituted) saturated linear alkyl groups include, but are not limited to, methyl (C_1), ethyl (C_2), n-propyl (C_3), n-butyl (C_4), n-pentyl (amyl) (C_5), n-hexyl (C_6), and n-heptyl (C_7).

Examples of (unsubstituted) saturated branched alkyl groups include iso-propyl (C_3), iso-butyl (C_4), sec-butyl (C_4), tert-butyl (C_4), iso-pentyl (C_5), and neo-pentyl (C_5).

Examples of (unsubstituted) saturated alkylene groups include, but are not limited to, methylene (C_1), ethylene (C_2), propylene (C_3), butylene (C_4), pentylene (C_5), hexylene (C_6), and heptylene (C_7).

Examples of (unsubstituted) saturated linear alkylene groups include, but are not limited to, methylene (C_1), ethylene (C_2), n-propylene (C_3), n-butylene (C_4), n-pentylene (amylene) (C_5), n-hexylene (C_6), and n-heptylene (C_7).

Examples of (unsubstituted) saturated branched alkyl groups include iso-propylene (C_3), iso-butylene (C_4), sec-butylene (C_4), tert-butylene (C_4), iso-pentylene (C_5), and neo-pentylene (C_5).

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 C_{2-4} alkenyl, C_{2-7} alkenyl, C_{2-20} alkenyl.

Examples of (unsubstituted) unsaturated alkenyl groups include, but are not limited to, ethenyl (vinyl, -CH=CH_2), 1-propenyl (-CH=CH-CH_3), 2-propenyl (allyl, -CH_2-CH=CH_2), isopropenyl (1-methylvinyl, -C(CH_3)=CH_2), butenyl (C_4), pentenyl (C_5), and hexenyl (C_6).

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.

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.

Examples of (unsubstituted) unsaturated alkynyl groups include, but are not limited to, ethynyl (ethinyl, -C≡CH) and 2-propynyl (propargyl, -CH_2-C≡CH).

Alkynylene: The term "alkynyl", 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.

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.

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 "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 C_{3-20} cycloalkylene, C_{3-15} cycloalkylene, C_{3-10} cycloalkylene, C_{3-7} cycloalkylene.

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 C_{3-20} cyclic alkylenes, C_{3-15} cyclic alkylenes, C_{3-10} cyclic alkylenes, C_{3-7} cyclic alkylenes.

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

saturated monocyclic hydrocarbon compounds:

cyclopropane (C_3), cyclobutane (C_4), cyclopentane (C_5), cyclohexane (C_6), cycloheptane (C_7), methylcyclopropane (C_4), dimethylcyclopropane (C_5),

methylcyclobutane (C_5), dimethylcyclobutane (C_6), methylcyclopentane (C_6), dimethylcyclopentane (C_7), methylcyclohexane (C_7), dimethylcyclohexane (C_8), menthane (C_{10});

unsaturated monocyclic hydrocarbon compounds:

cyclopropene (C_3), cyclobutene (C_4), cyclopentene (C_5), cyclohexene (C_6), methylcyclopropene (C_4), dimethylcyclopropene (C_5), methylcyclobutene (C_5), dimethylcyclobutene (C_6), methylcyclopentene (C_6), dimethylcyclopentene (C_7), methylcyclohexene (C_7), dimethylcyclohexene (C_8);

saturated polycyclic hydrocarbon compounds:

thujane (C_{10}), carane (C_{10}), pinane (C_{10}), bornane (C_{10}), norcarane (C_7), norpinane (C_7), norbornane (C_7), adamantane (C_{10}), decalin (decahydronaphthalene) (C_{10});

unsaturated polycyclic hydrocarbon compounds:

camphene (C_{10}), limonene (C_{10}), pinene (C_{10});

polycyclic hydrocarbon compounds having an aromatic ring:

indene (C_9), indane (e.g., 2,3-dihydro-1H-indene) (C_9), tetralin (1,2,3,4-tetrahydronaphthalene) (C_{10}), acenaphthene (C_{12}), fluorene (C_{13}), phenalene (C_{13}), acephenanthrene (C_{15}), aceanthrene (C_{16}), cholanthrene (C_{20}).

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.

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 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.

When referring to heterocyclyl or heterocyclylene groups, the prefixes (e.g. C_{3-20}, C_{3-7}, C_{5-6}, etc.) denote the number of ring atoms, or range of number of ring atoms, whether carbon atoms or heteroatoms. For example, the term "C_{5-6} heterocyclyl", as

used herein, pertains to a heterocyclyl group having 5 or 6 ring atoms. Examples of groups of heterocyclyl groups include C_{3-20} heterocyclyl, C_{5-20} heterocyclyl, C_{3-15} heterocyclyl, C_{5-15} heterocyclyl, C_{3-12} heterocyclyl, C_{5-12} heterocyclyl, C_{3-10} heterocyclyl, C_{5-10} heterocyclyl, C_{3-7} heterocyclyl, C_{5-7} heterocyclyl, and C_{5-6} heterocyclyl.

Similarly, the term "C_{5-6} heterocyclylene", as used herein, pertains to a heterocyclylene group having 5 or 6 ring atoms. Examples of groups of heterocyclylene groups include C_{3-20} heterocyclylene, C_{5-20} heterocyclylene, C_{3-15} heterocyclylene, C_{5-15} heterocyclylene, C_{3-12} heterocyclylene, C_{5-12} heterocyclylene, C_{3-10} heterocyclylene, C_{5-10} heterocyclylene, C_{3-7} heterocyclylene, C_{5-7} heterocyclylene, and C_{5-6} heterocyclylene.

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

N_1: aziridine (C_3), azetidine (C_4), pyrrolidine (tetrahydropyrrole) (C_5), pyrroline (e.g., 3-pyrroline, 2,5-dihydropyrrole) (C_5), 2H-pyrrole or 3H-pyrrole (isopyrrole, isoazole) (C_5), piperidine (C_6), dihydropyridine (C_6), tetrahydropyridine (C_6), azepine (C_7);

O_1: oxirane (C_3), oxetane (C_4), oxolane (tetrahydrofuran) (C_5), oxole (dihydrofuran) (C_5), oxane (tetrahydropyran) (C_6), dihydropyran (C_6), pyran (C_6), oxepin (C_7);

S_1: thiirane (C_3), thietane (C_4), thiolane (tetrahydrothiophene) (C_5), thiane (tetrahydrothiopyran) (C_6), thiepane (C_7);

O_2: dioxolane (C_5), dioxane (C_6), and dioxepane (C_7);

O_3: trioxane (C_6);

N_2: imidazolidine (C_5), pyrazolidine (diazolidine) (C_5), imidazoline (C_5), pyrazoline (dihydropyrazole) (C_5), piperazine (C_6);

N_1O_1: tetrahydrooxazole (C_5), dihydrooxazole (C_5), tetrahydroisoxazole (C_5), dihydroisoxazole (C_5), morpholine (C_6), tetrahydrooxazine (C_6), dihydrooxazine (C_6), oxazine (C_6);

N_1S_1: thiazoline (C_5), thiazolidine (C_5), thiomorpholine (C_6);

N_2O_1: oxadiazine (C_6);

O_1S_1: oxathiole (C_5) and oxathiane (thioxane) (C_6); and,

$N_1O_1S_1$: oxathiazine (C_6).

Examples of substituted (non-aromatic) monocyclic heterocyclyl and heterocyclylene groups include those derived from saccharides, in cyclic form, for example, furanoses (C_5), such as arabinofuranose, lyxofuranose, ribofuranose, and xylofuranse, and pyranoses (C_6), such as allopyranose, altropyranose, glucopyranose, mannopyranose, gulopyranose, idopyranose, galactopyranose, and talopyranose.

C_{5-20} aryl: The term "C_{5-20} aryl", as used herein, pertains to a monovalent moiety obtained by removing a hydrogen atom from an aromatic ring atom of a C_{5-20} 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 "C_{5-20} carboaryl" group.

C_{5-20} arylene: The term "C_{5-20} arylene", as used herein, pertains to a divalent moiety obtained by removing a hydrogen atom from each of two adjacent ring atoms of a C_{5-20} 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 "C_{5-20} carboarylene" group.

Examples of C_{5-20} aryl and C_{5-20} arylene groups which do not have ring heteroatoms (i.e. C_{5-20} carboaryl and C_{5-20} carboarylene groups) include, but are not limited to,

those derived from benzene (i.e. phenyl) (C_6), naphthalene (C_{10}), anthracene (C_{14}), phenanthrene (C_{14}), and pyrene (C_{16}).

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 "C_{5-20} heteroaryl" or "C_{5-20} heteroarylene" group, wherein "C_{5-20}" 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 C_{5-20} heteroaryl and C_{5-20} heteroarylene groups include, but are not limited to, C_5 heteroaryl and C_5 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 C_6 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.

Examples of C_{5-20} heteroaryl and C_{5-20} heteroarylene groups which comprise fused rings, include, but are not limited to, C_9 heteroaryl and C_9 heteroarylene groups derived from benzofuran, isobenzofuran, benzothiophene, indole, isoindole; C_{10} heteroaryl and C_{10} heteroarylene groups derived from quinoline, isoquinoline, benzodiazine, pyridopyridine; C_{14} heteroaryl and C_{14} heteroarylene groups derived from acridine and xanthene.

Bi-C_{5-20} aryl: The term "bi-C_{5-20} aryl", as used herein, pertains to a divalent moiety obtained by removing a hydrogen atom from two aromatic ring atoms of a bi-C_{5-20} aromatic compound, said compound comprising two C_{5-20} aromatic moieties joined by a single bond, each moiety 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 "C_{5-20} carboaryl" group. Examples of bi-

C_{5-20} aryl groups which do not have ring heteroatoms (i.e. bi-C_{5-20} carboaryl) include, but are not limited to, those where both moieties are derived from benzene (i.e. bi-phenyl)(C_6), naphthalene (i.e. bi-naphyhyl)(C_{10}), anthracene (C_{14}), phenanthrene (C_{14}), and pyrene (C_{16}).

Alternatively, the ring atoms of one or both moieties 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 "bi-C_{5-20} heteroaryl" group if both moieties contain ring heteroatoms or a "bi-C_{5-20} carboaryl-C_{5-20} heteroaryl" group if only one moiety comprises a ring heteroatom. "C_{5-20}" 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.

A "bi-C_{5-7} aryl" group is one where both moieties are C_{5-7} aryl groups. Likewise, a "bi-C_{9-10} aryl" group is one where both moieties are C_{9-10} aryl groups

Bisoxy-C_{1-3} alkylene: -O-$(CH_2)_m$-O-, where m is 1 to 3.

The above alkyl, alkylene, bisoxyalkylene, cyclic alkylene, heterocyclyl, heterocyclylene, aryl, bi-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.

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

Hydroxy: -OH.

Ether: -OR, wherein R is an ether substituent, for example, a C_{1-7} alkyl group (also referred to as a C_{1-7} alkoxy group), a C_{3-20} heterocyclyl group (also referred to as a C_{3-20} heterocyclyloxy group), or a C_{5-20} aryl group (also referred to as a C_{5-20} aryloxy group), preferably a C_{1-7} alkyl group.

Nitro: -NO_2.

Cyano (nitrile, carbonitrile): -CN.

Acyl (keto): -C(=O)R, wherein R is an acyl substituent, for example, H, a C_{1-7} alkyl group (also referred to as C_{1-7} alkylacyl or C_{1-7} alkanoyl), a C_{3-20} heterocyclyl group (also referred to as C_{3-20} heterocyclylacyl), or a C_{5-20} aryl group (also referred to as C_{5-20} arylacyl), preferably a C_{1-7} alkyl group. Examples of acyl groups include, but are not limited to, -C(=O)CH_3 (acetyl), -C(=O)CH_2CH_3 (propionyl), -C(=O)$C(CH_3)_3$ (pivaloyl), and -C(=O)Ph (benzoyl, phenone).

Carboxy (carboxylic acid): -COOH.

Ester (carboxylate, carboxylic acid ester, oxycarbonyl): -C(=O)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, -C(=O)OCH_3, -C(=O)OCH_2CH_3, -C(=O)$OC(CH_3)_3$, and -C(=O)OPh.

Amido (carbamoyl, carbamyl, aminocarbonyl, carboxamide): -C(=O)NR^1R^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, -C(=O)NH_2, -C(=O)$NHCH_3$, -C(=O)$N(CH_3)_2$, -C(=O)$NHCH_2CH_3$, and -C(=O)$N(CH_2CH_3)_2$, 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.

Amino: -NR^1R^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, -NH_2, -$NHCH_3$, -$NHCH(CH_3)_2$, -$N(CH_3)_2$, -$N(CH_2CH_3)_2$, and -NHPh. Examples of cyclic amino groups include, but are not limited to, aziridinyl, azetidinyl, 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.

Onium group: $-NR_3$ (ammonium group), $-SR_2$, $-PR_3$ and $-SbR_3$, 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 one or two R can be hydrogen. Two or three of the onium substituents may join together to form cyclic or cage-like structures.

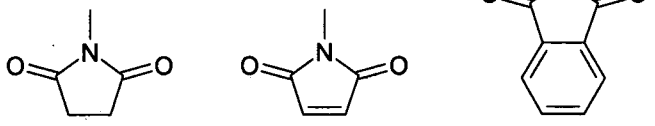
Ammonium group: $-NR^{N1}R^{N2}R^{N3}$, wherein R^{N1}, R^{N2} and R^{N3} are independently ammonium substituents, for example, a C_{1-7} alkyl group, a C_{3-20} heterocyclyl group, or a C_{5-20} aryl group and where one or two of R^{N1}, R^{N2} and R^{N3} may also be H. One of R^{N1}, R^{N2} and R^{N3} may be a C_{1-3} alkoxy ($-(CH_2)_{1-3}-OH$)group. Two or three of the ammonium substituents may join together to form cyclic or cage-like structures. Examples of ammonium groups 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 $-NH_2Ph$.

Onium linking group: $-NR_2R'-$ (ammonium linking group), $-SRR'-$, $-PR_2R'-$ and $-SbR_2R'-$, 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 one or two R can be hydrogen. Two of the onium substituents may join together to form cyclic or cage-like structures. R' is a divalent onium 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} alkyloxylene ($-(CH_2)_{1-3}-O-$) group.

Ammonium linking group: $-NR^{N1}R^{N2}R^{N4}-$, wherein R^{N1} and R^{N2} 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 R^{N1} and R^{N2} may also be H. The two ammonium substituents may join together to form a cyclic structure. R^{N4} 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} alkyloxylene ($-(CH_2)_{1-3}-O-$) group. Examples of ammonium linking groups 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 $-NHPh(CH_2)-$.

Acylamido (acylamino): $-NR^1C(=O)R^2$, 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, -NHC(=O)CH_3 , -NHC(=O)CH_2CH_3, and -NHC(=O)Ph. R^1 and R^2 may together form a cyclic structure, as in, for example, succinimidyl, maleimidyl, and phthalimidyl:



succinimidyl maleimidyl phthalimidyl

Ureido: -N(R^1)CONR^{2}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, -NHCONH_2, -NHCONHMe, -NHCONHEt, -NHCONMe_2, -NHCONEt_2, -NMeCONH_2, -NMeCONHMe, -NMeCONHEt, -NMeCONMe_2, -NMeCONEt_2 and -NHCONHPh.

Acyloxy (reverse ester): -OC(=O)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, -OC(=O)CH_3 (acetoxy), -OC(=O)CH_2CH_3, -OC(=O)C$(CH_3)_3$, -OC(=O)Ph, -OC(=O)C_6H_4F, and -OC(=O)CH_2Ph.

Thiol : -SH.

Thioether (sulfide): -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, -SCH_3 and -SCH_2CH_3.

Sulfoxide (sulfinyl): -S(=O)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, -S(=O)CH_3 and -S(=O)CH_2CH_3.

Sulfonyl (sulfone): $-S(=O)_2R$, 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, $-S(=O)_2CH_3$ (methanesulfonyl, mesyl), $-S(=O)_2CF_3$, $-S(=O)_2CH_2CH_3$, and 4-methylphenylsulfonyl (tosyl).

Thioamido (thiocarbamyl): $-C(=S)NR^1R^2$, 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, $-C(=S)NH_2$, $-C(=S)NHCH_3$, $-C(=S)N(CH_3)_2$, and $-C(=S)NHCH_2CH_3$.

Sulfonamino: $-NR^1S(=O)_2R$, 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, $-NHS(=O)_2CH_3$, $-NHS(=O)_2Ph$ and $-N(CH_3)S(=O)_2C_6H_5$.

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.

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 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 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 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 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 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 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 acetyl ester (-OC(=O)CH_3, -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 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 (-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-trimethylsilylethyloxy amide (-NH-Teoc), as a 2,2,2-trichloroethyloxy amide (-NH-Troc), as an allyloxy amide (-NH-Alloc), as a 2(-phenylsulphonyl)ethyloxy amide (-NH-Psec); or, in suitable cases (e.g., cyclic amines), as a nitroxide radical (>N-O•).

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 triC_{1-7}alkylsilyl-C_{1-7}alkyl ester; or a C_{5-20}aryl-C_{1-7}alkyl ester (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-$CH_2NHC(=O)CH_3$).

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

Catalysed reactions

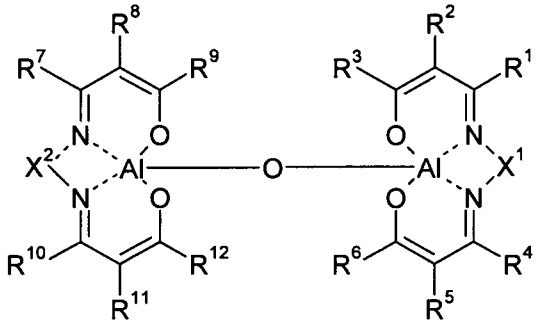
In one aspect of the present invention, there is provided a process for the production of cyclic carbonates comprising contacting an epoxide with carbon dioxide in the presence of a dimeric aluminium(acen) or aluminium(salacen) catalyst of formula I.

This reaction has the advantage that it may be carried out at easily accessible 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.

In particular embodiments of the invention, there is provided a dimeric aluminium catalyst of formula Ia:

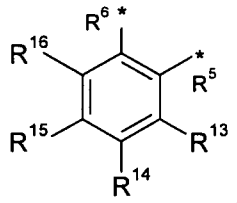


(Ia)

wherein:

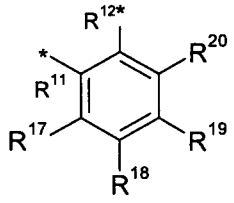
a) each of the substituents R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12}, is independently selected from H, halo, optionally substituted C_{1-20} alkyl (including CAr_3, where Ar is a C_{5-20} aryl group), optionally substituted C_{5-20} aryl, optionally substituted C_{3-20}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

b) R^5 and R^6 together with the carbon atoms to which they are attached form an optionally substituted benzene ring of formula:



, and

R^{11} and R^{12} together with the carbon atoms to which they are attached form an optionally substituted benzene ring of formula:



,

each of the substituents R^1, R^2, R^3, R^4, R^7, R^8, R^9, R^{10}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20}, 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_{9-10} arylene, bi-C_{5-7} aryl, bi-C_{9-10} aryl, C_{5-7} cyclic alkylene and C_{3-7} heterocyclylene, which may be optionally substituted.

In particular embodiments of the invention, there is provided a catalyst of formula (Ia) as defined above, except that:

(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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) is selected from L-A, where L is a single bond or a C_{1-10} alkylene group and A is an onium 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 forming part of an ammonium group 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)-O-, -C(=O)-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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) is L-A', where L is as defined above and A' is an onium 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'.

In some aspects of the invention, L is selected from a single bond and C_{1-7} alkylene.

In some embodiments of the invention, the aluminium(acen) or aluminium (salacen) catalyst of formula I or Ia is symmetrical, such that X^1=X^2, R^1=R^7, R^2=R^8, R^3=R^9, R^4=R^{10}, R^5=R^{11}, R^6=R^{12} and (if present) R^{13}=R^{17}, R^{14}=R^{18}, R^{15}=R^{19} and R^{16}=R^{20}. In some embodiments, it is preferred that R^1, R^4, R^7, and R^{10} are identical, R^2, R^5, R^8 and R^{11} are identical, and R^3, R^6, R^9, and R^{12} are identical.

In the embodiments of the invention where the aluminium(acen) or aluminium (salacen) catalyst of formula I is symmetrical then the alkylene group formed by R^2

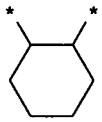
and R^3 will be identical to that formed by R^8 and R^9, and the alkylene group formed by R^5 and R^6 will be identical to that formed by R^{11} and R^{12}, if these groups are present.

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

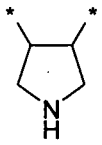
In some embodiments, X^1 and X^2 are the same.

In some embodiments, X^1 and X^2 are independently selected from a C_{2-5} alkylene chain, which is preferably unsubstituted, and a C_{1-3} bisoxylakylene chain, which is preferably unsubstituted. These groups can be represented as $-(CH_2)_n-$ or $-O-(CH_2)_p-O-$, 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 X^1 and X^2 are preferably selected from $-(CH_2)_n-$ (e.g. $-C_2H_4-$).

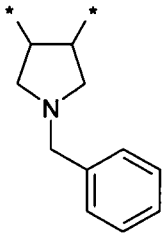
In other embodiments, X^1 and X^2 independently represent a divalent group selected from C_{5-7} arylene, C_{9-10} arylene, bi-C_{5-7} aryl, bi-C_{9-10} aryl, C_{5-7} cyclic alkylene and C_{3-7} heterocyclylene, which may be optionally substituted. Preferably X^1 and X^2 independently represent C_{5-7} cyclic alkylene, and more preferably C_6 cyclic alkylene. This group is preferably saturated, and therefore is the group:



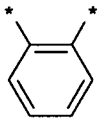
In other preferred embodiments, X^1 and X^2 independently represent C_{5-7} heterocyclene, and more preferably C_5 heterocyclene. One such preferred group is:



In this group, the nitrogen atom may be substituted, for example, by a C_{1-4} alkyl group (e.g. methyl) that may itself be substituted, for example, by a C_{5-7} aryl group (e.g. phenyl). Therefore a preferred group for X^1 and X^2 is:



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:



When X^1 and X^2 independently represent a divalent group selected from C_{5-7} arylene, C_{9-10} arylene, bi-C_{5-7} aryl, bi-C_{9-10} aryl, C_{5-7} cyclic alkylene and C_{3-7} heterocyclylene, they may preferably be unsubstituted. If they are 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.

In some embodiments, R^5 and R^6, and R^{11} and R^{12} do not form fused benzene rings.

In some embodiments, $R^1 = R^4 = R^7 = R^{10} = H$.

In some embodiments, $R^3 = R^6 = R^9 = R^{12} = H$.

In some embodiments, $R^1 = R^4 = R^7 = R^{10} = Me$.

In some embodiments, $R^3 = R^6 = R^9 = R^{12} = Me$.

In some embodiments, $R^2 = R^5 = R^8 = R^{11} = H$.

In particularly preferred embodiments of the present invention, $R^1 = R^4 = R^7 = R^{10} = Me$; $R^3 = R^6 = R^9 = R^{12} = Me$; and $R^2 = R^5 = R^8 = R^{11} = H$.

In some embodiments, $R^1 = R^7 = H$.

In some embodiments, $R^2 = R^8 = H$.

In some embodiments, $R^3 = R^9 = H$.

In some embodiments, $R^4 = R^{10} = H$.

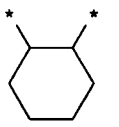
In some embodiments, R^5 and R^6 together with the atoms to which they are joined form a benzene ring, which is preferably unsubstituted.

In some embodiments, R^{11} and R^{12} together with the atoms to which they are joined form a benzene ring, which is preferably unsubstituted.

In particularly preferred embodiments of the present invention, $R^1 = R^7 = H$; $R^2 = R^8 = H$; $R^3 = R^9 = H$; $R^4 = R^{10} = H$; R^5 and R^6 together with the atoms to which they are joined form an unsubstituted benzene ring; and R^{11} and R^{12} together with the atoms to which they are joined form an unsubstituted benzene ring.

If R^2, R^5, R^8 and R^9 are selected from optionally substituted ester or optionally substituted acyl, the ester group may be an unsubstituted C_{1-7} alkyl ester, more preferably an unsubstituted C_{1-4} alkyl ester (e.g. ethyl ester), and the acyl group may be an unsubstituted C_{1-7} alkylacyl, more preferably an unsubstituted C_{1-4} alkylacyl (e.g. methyl acyl).

In further embodiments of the invention, $R^2 = R^5 = R^8 = R^{11} = -CO_2Me$. In these embodiments, it may be preferred that $R^1 = R^4 = R^7 = R^{10} = H$, and $R^3 = R^6 = R^9 = R^{12} = Me$. It may also or alternatively be preferred that X^1 and X^2 are $-C_2H_4-$ or:



If a pair of R^2 and R^3, R^5 and R^6, R^8 and R^9 and R^{11} and R^{12} together form a C_{2-4} alkylene chain, the chain may be unsubstituted.

In some embodiments, it is one or more of R^2, R^5, R^8 and R^{11} 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.
In some further embodiments, one of R^2, R^5, R^8 and R^{11} is -Q'-L-A or -Q'-L-A'. In some of these further embodiments, if one of these groups is -Q'-L-A', the other groups are -Q'-L-A. Alternatively, the other groups may be -Q'-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.
In some embodiments, those 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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) which do not comprise -L-A or -L-A' are independently selected (where appropriate) from H, C_{1-7} alkyl, ether and nitro. If none of the groups are -L-A or -L-A' then they all may be independently selected (where appropriate) from H, C_{1-7} alkyl, ether and nitro.

If a group selected from 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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) 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.

If a group selected from 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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) is C_{1-7} alkyl, it may be C_{1-4} alkyl, e.g. methyl, ethyl, propyl and butyl (preferably tert-butyl).

L is preferably unsubstituted.

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

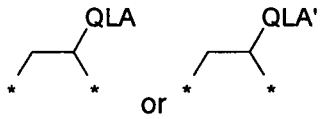
A may preferably be selected from ammonium groups, and in particular, those groups where R^{N1}, R^{N2} and R^{N3} are independently selected from C_{1-7} alkyl groups and C_{5-20} aryl groups, and where one or two of R^{N1}, R^{N2} and R^{N3} may also be H. Ammonium groups of particular interest in 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 $-NH_2Ph$.

A' may preferably be selected from ammonium linking group, and in particular those 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}

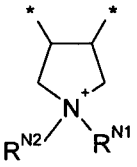
alkylene group. Ammonium linking groups of particular interest in the present invention include, but are not limited to, -NH(CH_3)(CH_2)-, -NH(CH(CH_3)$_2$)(C(CH_3)$_2$)-, -N(CH_3)$_2$(CH_2)-, -N(CH_2CH_3)$_2$(CH_2CH_2)-, and -NHPh(CH_2)-.

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:

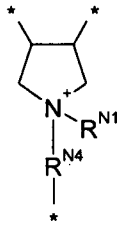


If X^1 or X^2 is a divalent C_{3-7} heterocyclene group containing a ring atom which is a quaternary nitrogen atom, then it is preferably of the formula:



R^{N1} and R^{N2} in the above group are independently selected from C_{1-7} alkyl groups (including, for example, those substituted by a C_6 aryl group) and C_{5-20} aryl groups, and where one of R^{N1} and R^{N2} may also be H. R^{N1} and R^{N2} groups of particular interest in above structure include, but are not limited to, -CH_3, -CH(CH_3)$_2$, and -CH_2Ph.

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:



Compounds of particular interest are 6, 7, 10 and 11.

The reaction may be carried out under solvent-free conditions, depending on the 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.

Reactions using the catalyst of the first aspect, and some reactions using the catalyst of the second aspect, require the addition of a co-catalyst, Y^-, and in particular MY, 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.

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. The amount of co-catalyst is preferably less than 2.5%, more preferably less than 1.0 mol% and most preferably less than 0.5 mol%. In some embodiments using a catalyst of the second aspect of the invention, no separate co-catalyst is present.

The above preferences may be combined with each other in any way that is appropriate.

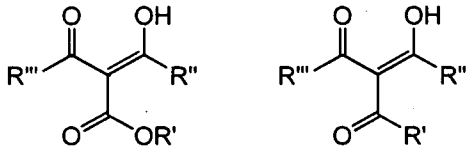
Manufacture of dimeric aluminium(acen) and aluminium(salacen) complexes

In a fourth aspect of the invention, there is provided a process for the production of dimeric aluminium(acen) and aluminium(salacen) catalysts of formula I.

When the catalyst of formula I comprises one or more onium group paired with a counterion, it may be synthesised from a precursor comprising the corresponding neutral groups (e.g. amine, sulphide, phosphine) by reaction with a organic halide (i.e. a C_{1-7} alkyl, C_{3-20} heterocyclyl or C_{5-20} aryl halide), or an organic group with another leaving group (e.g. tosylate).

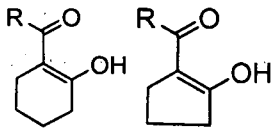
When the catalyst of formula I comprises an onium linking group bound to a solid support, it may be synthesised from a precursor catalyst comprising a corresponding neutral group (e.g. amine, sulphide, phosphine) by reaction with a halide derived solid support or a solid support derived with another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

In catalysts where at least one of R^2, R^5, R^8 and R^9 are optionally substituted ester or optionally substituted acyl groups, the ligands may be synthesised from precursors of formulae:



Such ligand synthesis is described, for example, in Yamada, *et al.*, *Bull. Chem. Soc. Jpn.*, **80(7)** (2007), 1391-1401.

In catalysts where at least one of the pairs of R^2 and R^3, R^5 and R^6, R^8 and R^9 and R^{11} and R^{12} are independently together form a C_{2-4} alkylene chain, 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, the ligands may be synthesised from precursors of formulae:



Such compounds are described, for example, in Barna and Robinson, *Tet Lett* **16** (1979), 1455-1458; Jones and Stokes, *Tet* **40(6)** (1984), 1051-1060; Kuhakarn, *et al.*, *Tet* **61** (2005), 8995-9000; Martins, *et al.*, *J Het Chem*, **33** (1996), 1223-1231.

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 (ATR) were recorded on a Nicolet380 FTIR spectrometer fitted with a 'Smart orbit' attachment.

NMR

All NMR spectra were recorded at ambient temperature on a Bruker Avance 300 spectrometer. The sample was dissolved in $CDCl_3$ unless specified otherwise.

Mass spectroscopy

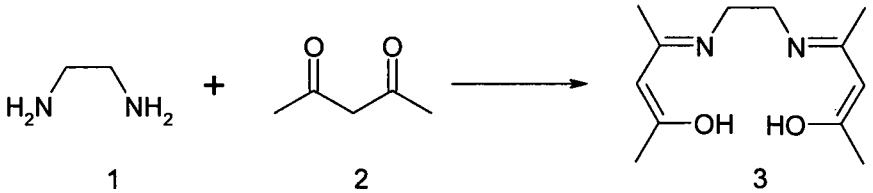
GCMS were recorded on a Varian CP-800-SATURN 2200 GC/MS ion-trap mass spectrometer using a FactorFour (VF-5 ms) capillary column (30 m x 0.25 mm) with

helium as the carrier gas. The conditions used were: initial temperature 60°C, hold at initial temperature for 3 minutes then ramp rate 15°C/min to 270°C; hold at final temperature for 5 minutes. For the first 3.50 minutes, the eluent was routed away from the mass detector. Subsequently, the detector was operated in full EI scan mode. Calibration was carried out by using a 50:50 mixture of pure isolated carbonate and reagent grade styrene oxide. Peak integration was found to be virtually 50% for each component.

Low and high resolution electrospray spectra were recorded on a Waters LCT Premier mass spectrometer.

Synthesis of Key Intermediates

Acen ligand (3)



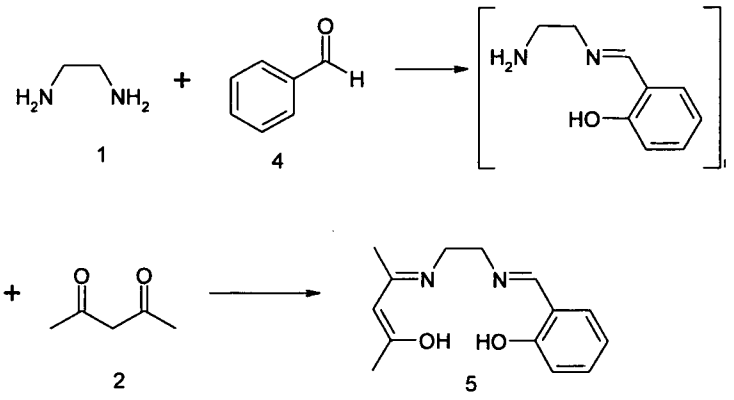
1 2 3

Prepared by the method of McCarthy, P.J., *et al., J. Am.Chem. Soc.,* **1955**, *77*, 5820. 1,2-Diaminoethane (1)(3.0 g, 3.3 mL, 49.9 mmol) was dissolved in ethanol (70 mL) and acetylacetone (2)(10.3 mL, 99.8 mmol) was added in a steady stream over a period of about 10 minutes whilst stirring the reaction mixture. The reaction was refluxed for 3 hours. After cooling, evaporation of the solvent *in vacuo* left a yellow solid which was purified by the addition of diethyl ether (ca. 100 mL). The desired ligand (3)(7.3 g, 32.4 mmol, 65%) was obtained as an off-white crystalline solid by suction filtration.

mp 116-118°C

$\delta_H(CDCl_3)$ 4.97 (2H, s), 3.4-3.3 (4H, m), 1.97 (6H, s), 1.88 (6H, s)

Salacen ligand (5)

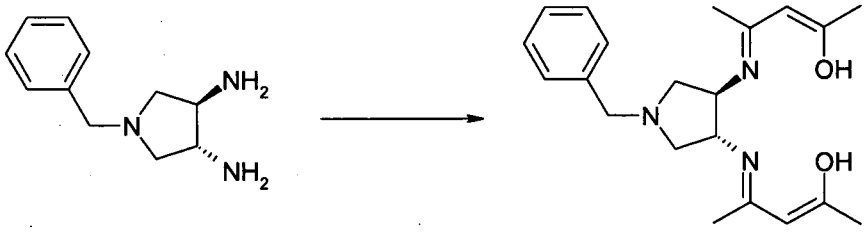


Preparation based on the method reported by Phan, N.T.S., *et al.*, *Dalton Trans.*, **2004**, 1348. Ethylene diamine (1)(2.7 g, 45.0 mmol) was dissolved in dichloromethane (50 mL) and salicylaldehyde (4)(5.0g, 41.0 mmol) was added in a slow stream while stirring the reaction. The resulting yellow mixture was stirred at ambient temperature for a further 30 minutes. Acetyl acetone (2)(4.5 g, 45.0 mmol) was then added and the reaction mixture heated to reflux with stirring for one hour. The reaction was then allowed to cool to room temperature and was stirred overnight. Evaporation of the solvent gave a yellow solid which was taken up in the minimum volume of hot methanol required to dissolve all the solids (ca. 10 mL) and then cooled. A yellow crystalline precipitate formed which was filtered and identified as salen. The mother liquor was evaporated under vacuum to give the desired ligand (5) as a yellow / amber powder (2.7 g, 11.0 mmol, 27%).

Mp 122-126°C

$\delta_H(CDCl_3)$ 8.35 (1H, s), 7.3-7.2 (2H, m), 7.0-6.9 (2H, m), 4.93 (1H, s), 3.75 (2H, m), 3.41 (2H, m), 1.99 (3H, s), 1.96 (3H, s).

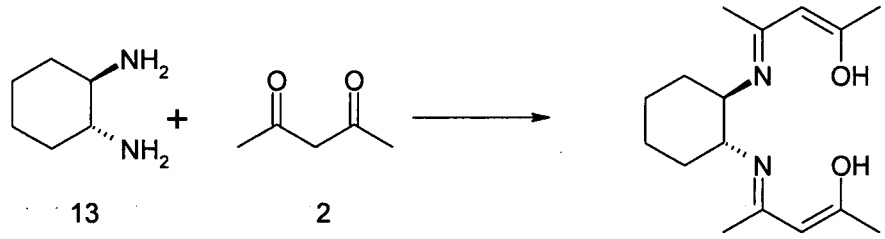
Pyrrolidine-based diamine acen ligand (9)



Diamine **8** was prepared by the literature method (Hato, Y.; Kano, T.; Maruoka, K. *Tetrahedron Letters*, **2006**, 8467) from the precursor diazido species by hydrogenation (10atm H_2, 3.5 days) over 10% palladium on carbon in ethanol

(50mL). The resulting product **8** (as a solution in ethanol) was used directly with 2,4-pentanedione (0.3mmol, 1.6mL) and heated at reflux for 18 hours. The solvent was evaporated and the resulting residue taken up in dichloromethane (50mL). The organic solution was washed with water (3 x 20mL) and brine (20mL) and dried over sodium sulphate. Evaporation of the dichloromethane gave a beige/yellow solid **9** (0.30g, 0.84mmol, 62%). ^{1}H-NMR ($CDCl_3$) δ_H: 1.79-1.84 (2H, m), 1.91 (6H, s), 2.10 (6H, s), 2.74-2.79 (2H, m), 3.56 (2H, s), 3.76 (2H, m), 4.82 (2H, m), 7.15-7.27 (5H, m). ^{13}C-NMR δ_C: 18.6, 30.2, 53.6, 62.1, 65.8, 68.0, 127.1, 128.5, 129.0, 142.0, 157.3, 204.2. m.p. 154-159°C.

Cyclohexane-based diamine acen ligand (14)

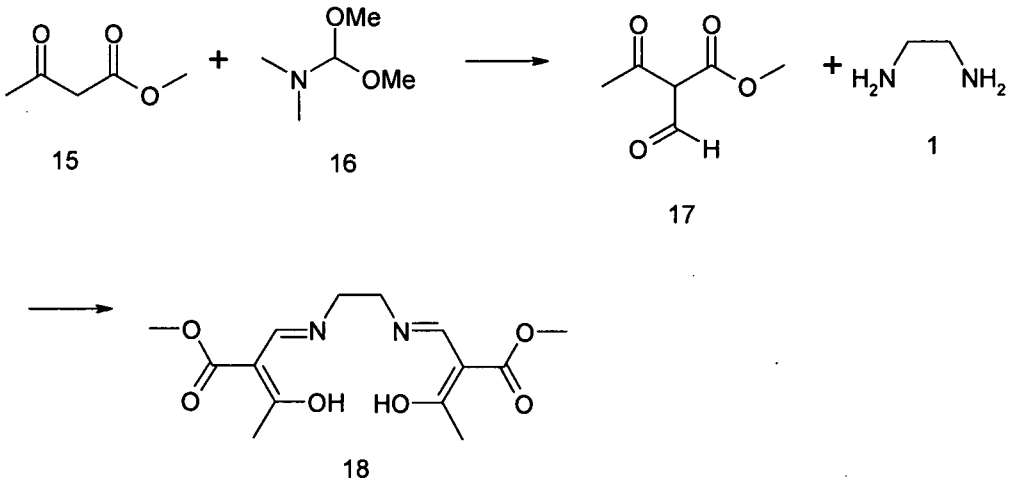


13 2 14

Compound 14 is disclosed in Pang, X., *et al. Journal of Organometallic Chemistry 692* (**2007**) 5605–5613.

(*R*,*R*)-1,2-diaminocyclohexane dihydrochloride (13)(3.0 g, 16.0 mmol,) and sodium methoxide (1.7 g, 32.0 mmol) were added to a 1:1 mixture of methanol and ethanol (50 mL) and heated to reflux with stirring for 20 minutes. Acetylacetone (2)(3.3 mL, 32.0 mmol) was then added and the reaction refluxed for 18 hours. The solvent was then evaporated *in vacuo* and the residue washed with diethyl ether (3 x 50 mL) to give the ligand as a pale yellow powder (3.6 g, 13.0 mmol, 81%).

Acen methyl ester ligand (18)



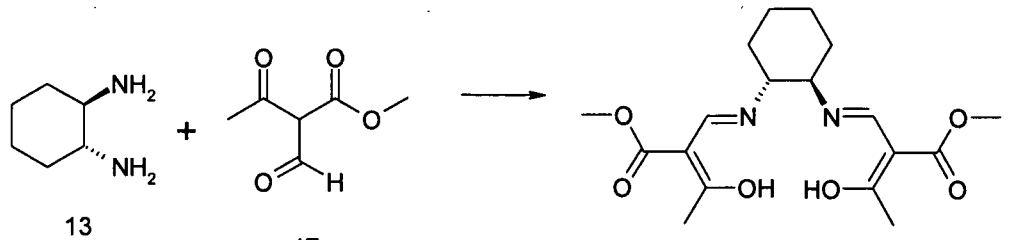
15 16 17 1

18

Compound 14 is disclosed in Mukaiyama, T. *et al. Chemistry Letters* **1993**, 327-330. Methyl acetoacetate (15)(4.6 mL, 43.0 mmol) and dimethylformamide dimethylacetal (5.7 mL, 43.0 mmol) were stirred at ambient temperature for two hours during which time the reaction turned from colourless to orange. Then, a 2M aqueous solution of sodium hydroxide (50 mL) was added and the reaction stirred for a further two hours during which time the solution became yellow. The reaction was poured into a separating funnel and water (50 mL) and dichloromethane (50 mL) were added and the aqueous phase neutralized with 1M aqueous hydrochloric acid. The product was extracted using further washings of dichloromethane (5 x 50mL), dried with sodium sulphate, filtered and evaporated *in vacuo*. The resulting bright yellow oil (17)(6.0 g) became red/orange on standing and was used directly in the next step without further purification.

The methyl 2-formyl 3-oxobutanoate (17)(6.0 g) was dissolved in ethanol (50 mL) and 1,2-diaminoethane (1)(1.4 mL, 21.5 mmol) was added. A yellow precipitate formed immediately and the reaction was allowed to stir for one hour at ambient temperature. The solvent was then evaporated *in vacuo* and the resulting material washed with diethyl ether (2 x 30mL) to give the acen ligand (18) as a yellow powder (6.1 g, 20.0 mmol, 91%). Mp >160°C (decomp.), ν_{max}(ATR) 3400-2600 br, 3244 w, 2955 w, 1702 s and 1622 cm^{-1} s; ^1H NMR ($CDCl_3$): 11.06 (2H, br), 7.89 (1H, s), 7.85 (1H, s), 3.70 (6H, s), 3.5-3.6 (4H, m), 2.46 (6H, s).

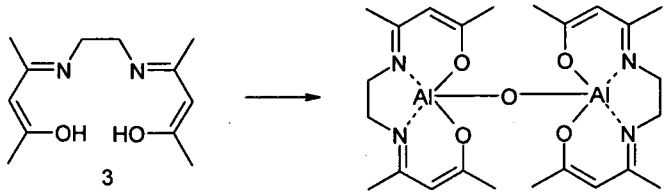
Cyclohexane-based acen methyl ester ligand (18)



13 17 19

(*R*,*R*)-1,2-diaminocyclohexane dihydrochloride (13)(3.0 g, 16.0 mmol) and sodium methoxide (1.7 g, 32.0 mmol) were added to a 1:1 mixture of methanol and ethanol (50 mL) and heated to reflux with stirring for 20 minutes. Methyl 2-formyl 3-oxobutanoate (17)(4.6 g, 32.0 mmol) was dissolved in ethanol (40 mL) and added to the refluxing solution of diamine. The reaction was allowed to stir under reflux for 20 hours during which time the solution became yellow. The solvent was then evaporated *in vacuo* giving an orange gel which was rinsed with hexane (2 x 30 mL) to give the ligand as a yellow oil (5.1 g, 14.0 mmol, 87%). $[\alpha]_D^{23}$ -524 (c = 0.1, MeCN); ν_{max}(ATR) 3400-2400 br, 2943 m, 2864 m, 1696 m and 1632 cm^{-1} s; ^1H NMR ($CDCl_3$): 10.93 (2H, br), 8.31 (2H, br s), 3.61 (6H, s), 3.1-3.3 (2H, m), 2.42 (6H, s), 1.9-1.7 (4H, m), 1.4-1.2 (4H, m).

Example 1



3 6

Acen ligand (3)(1.0 g, 4.5 mmol) was dissolved in toluene (25 mL) and heated to reflux under a nitrogen atmosphere. Aluminium triethoxide (1.5 g, 8.9 mmol) was then added and the reaction refluxed for 4 hours with stirring. The toluene was then removed by evaporation *in vacuo* and the resulting material taken up in dichloromethane (50 mL) and washed with water (3 x 20 mL). Evaporation of the organic layer gave a yellow powder to which was added diethyl ether (30 mL). The desired complex (6)(1.0 g, 2.0 mmol, 86%) was obtained as an off-white / light yellow crystalline solid by suction filtration.

mp: decomp >270°C.

υ_{max}(ATR) 1605 (m), 1522 (s) and 1419 cm^{-1} (m).

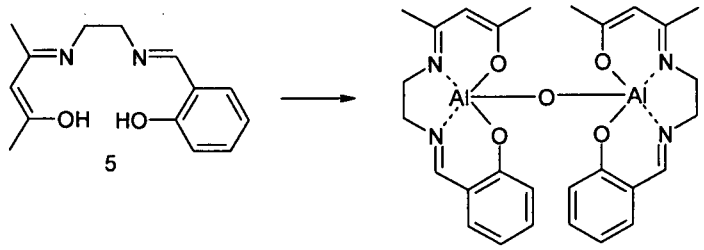
$\delta_H(CDCl_3)$ 5.11 (4H, s), 3.7-3.4 (8H, m), 2.03 (12H, s), 1.99 (12H, s).

$\delta_C(CDCl_3)$ 199.4, 177.4, 99.8, 46.2, 25.6, 21.7.

m/z(ES) 515.2 (MH^+), 281.1.

Found: 515.2358, $C_{24}H_{37}N_4O_5Al_2$ (MH^+) requires 515.2395.

Example 2



5 7

Salacen ligand (5)(1.0 g, 4.1 mmol) was dissolved in toluene (40 mL) and heated to reflux. Aluminium triethoxide (1.3 g, 8.3 mmol) was added and the reaction refluxed for four hours under a nitrogen atmosphere. The solution was allowed to stir and cool to room temperature overnight. The solvent was evaporated under vacuum and the resulting material taken up in dichloromethane (50 mL) and washed with water (3 x 20 mL). Diethyl ether (ca. 25 mL) was added to the resulting residue after evaporation of the solvent. The flask was cooled in ice and a yellow precipitate formed and was collected by filtration to give the desired complex (7) as a light yellow solid (0.95 g, 1.7 mmol, 84%).

mp: decomp >230°C.

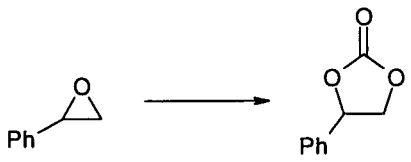
υ_{max}(ATR) 1637 (m), 1603 (m), 1526 (m), 1478 (m), 1455 (m) and 1408 cm^{-1} (w).

m/z(ES) 559.2 (MH^+), 537.2, 581.2.

Found: 559.2083, $C_{28}H_{33}N_4O_5Al_2$ (MH^+) requires 559.2082.

Example 3

(i)



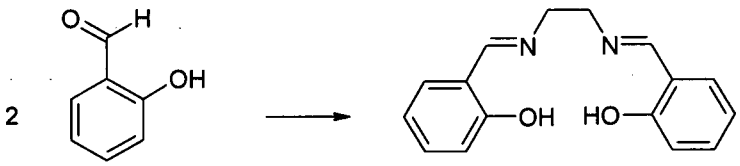
Bimetallic aluminium(acen) complex (6)(22 mg, 0.043 mmol) was weighed into a glass sample vial to which tetra-n-butyl ammonium bromide (TBAB) (13.5 mg, 0.042 mmol) was added. The vial was placed into a sealed flask containing a second vial filled with solid CO_2 pellets. The pressure of the system was regulated with a balloon.

After saturation of the reaction vessel with CO_2 gas, styrene oxide (0.2 g, 1.7 mmol) was added via a syringe to the catalyst-TBAB mixture. The reaction was stirred at 30°C for 24 hours. Samples were removed by a syringe and analysed by gas chromatography (or ^{1}H NMR spectroscopy) after 3 hours (33% conversion of styrene oxide to styrene carbonate), 6 hours (52% conversion of styrene oxide to styrene carbonate) and 24 hours (85% conversion of styrene oxide to styrene carbonate). After this time was the reaction was worked up and an isolated yield of 81% was obtained.

Styrene carbonate: mp 54-56°C. $\delta_H(CDCl_3)$ 7.4-7.3 (5H, m), 5.67 (1H, t *J* 8.0 Hz), 4.79 (1H, t *J* 8.3 Hz), 4.33 (1H, t *J* 8.0 Hz).

(ii) Using the same procedure with various epoxides, the following results were obtained with the aluminium(acen) complex(6) and aluminium(salacen) complex(7) and for comparison aluminium(salen) complex(C1) which was synthesised as follows:

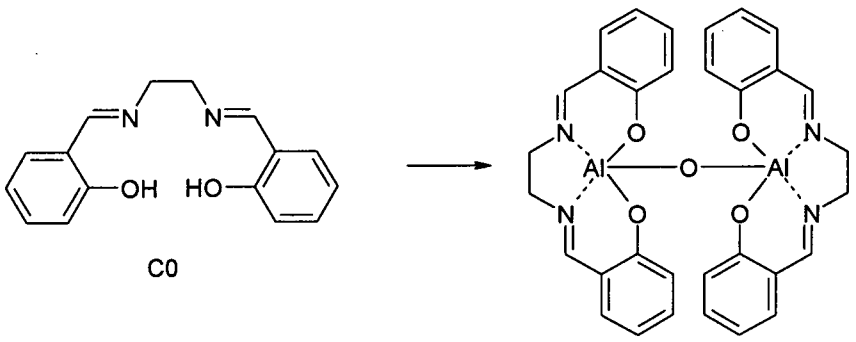
(a)



C0

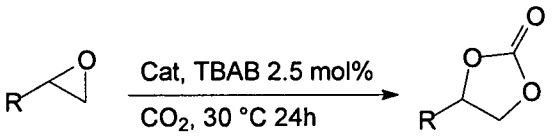
Ethylenediamine (50 mmol, 3.3 mL) was added via a syringe to a stirred solution of salicylaldehyde (100 mmol, 10.5 mL) in ethanol (100 mL). A yellow precipitate formed immediately. The reaction mixture was refluxed for 3 hours and the solvent was then removed *in vacuo* to leave a yellow crystalline solid which was washed with diethyl ether (*ca.* 100 mL) to give salen ligand (C0) (12.0 g, 90%). Mp. 126-130 °C. ^{1}H NMR 3.96 (4H, s, CH_2CH_2), 6.87 (2H, t *J* = 8.4 Hz, 2 x H_{Ar}), 6.97 (2H, t *J* = 8.7 Hz, 2 x H_{Ar}), 7.2-7.3 (4H, m, 4 x H_{Ar}), 8.38 (2H, s, 2 x CH=N), 13.23 (2H, s, 2 x OH).

(b)



C0 C1

Salen ligand (C0) (1.0 g, 3.9 mmol) and aluminium triethoxide (1.2 g, 7.4 mmol) were dissolved in dry toluene (25 mL). The reaction mixture was refluxed for 4 hours after which the toluene was evaporated and the resulting yellow residue taken up in dichloromethane and washed with water (3 x 100 mL) and saturated brine (100 mL). After evaporation of the organic phase, a light yellow powder was obtained which was washed with diethyl ether (*ca.* 50 mL) and dried to give salen complex (C1) (1.2 g, 49%). ^{1}H NMR 3.87 (8H, s, 2 x CH_2CH_2), 6.7-6.9 (8H, m, 8 x H_{Ar}), 7.1-7.3 (8H, m, 8 x H_{Ar}), 8.29 (4H, s, 4 x CHN). ^{13}C NMR 60.14, 65.09, 117.36, 119.00, 131.81, 132.74, 161.46,166.85. m/z(ESI) Found: 603.1775 $C_{32}H_{28}N_4O_5Al_2$ (MH^+), Requires 603.1769.



Catalyst	Substrate (R-)	Conversion %		
		3h	6h	24h
6	Ph-	33	52	85 (81)[b]
7		60	72	93
C1		81	93	100
6	$CH_3(CH_2)_3$-	97	97	100 (94)[b]
7		95	99	100
6	$CH_3(CH_2)_7$-	31	48	92 (89)[b]

7		43	59	99
6	$HOCH_2$-	33	67	98 (90)[b]
7		48	63	100
6	$ClCH_2$-	89	100	100 (91)[b]
7		76	98	100
6[a]	CH_3-	42	52	73 (70)[b]
7[a]		39	42	70
6[c]	H-			(58)[b]
7[c]				(100)[b]

a) Reaction was carried out at 0 °C. b) Isolated yield in brackets. c) Reactions were carried out in a stainless steel reactor with CO_2 under pressure (<3 bar).

GC Retention times:

Styrene oxide (7.35 mins), styrene carbonate (12.08 mins)

Hexene oxide (3.56 mins), hexene carbonate (9.80 mins)

Decene oxide (8.98 mins), decene carbonate (13.40 mins)

Propylene carbonate (5.26 mins)

Ethylene carbonate (5.98 mins)

NMR Data for carbonates: $\delta_H(CDCl_3)$:

1,2-Hexene carbonate: $\delta_H(CDCl_3)$ 4.65 (1H, m) 4.49 (1H, t *J* 7.6 Hz), 4.01 (1H, t *J* 7.1 Hz), 1.7-1.6 (2H, m), 1.4-1.3 (4H, m), 0.89 (3H, t *J* 6.6 Hz).

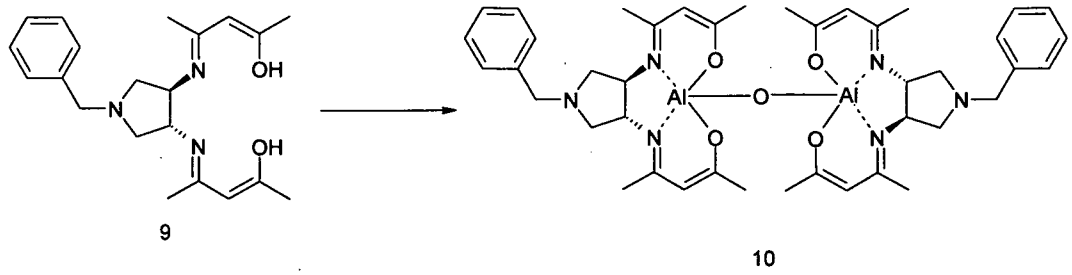
1,2-Decene carbonate: $\delta_H(CDCl_3)$ 4.7-4.6 (1H, m), 4.49 (1H, t *J* 8.1 Hz), 4.03 (1H, t *J* 7.5 Hz), 1.24 (14H, m), 0.85 (3H, t *J* 6.6Hz).

Propylene carbonate: $\delta_H(CDCl_3)$ 4.8-4.7 (1H, m), 4.55 (1H, t *J* 8.4 Hz), 4.02 (1H, dd *J* 8.4, 7.3 Hz), 1.46 (3H, d *J* 6.3 Hz).

Glycidol carbonate: 4.8-4.7 (1H, m), 4.5-4.4 (2H, m), 4.00 (1H, dd *J* 3.2, 12.9 Hz), 3.75 (1H, dd *J* 3.5, 12.7 Hz).

Epichlorohydrin carbonate: 5.0-4.9 (1H, m), 4.60 (1H, t *J* 8.7 Hz), 4.40 (1H, dd *J* 8.7, 5.7 Hz), 3.8-3.6 (2H, m).

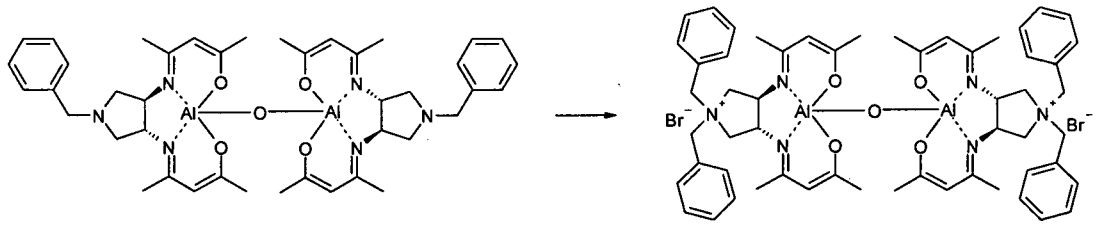
Example 4



9 10

Ligand **9** (0.84mmol, 0.30g) was dissolved in dry toluene (60mL) and heated to reflux. Aluminium triethoxide (1.68mmol, 0.27g) was added and heated for 24 hours. The resulting solution was washed with water (3 x 15mL) and brine (15mL) and dried over sodium sulphate. Evaporation yielded complex **10** as a yellow powder (0.32mmol, 0.24g, 75%). ^{1}H-NMR ($CDCl_3$) δ_H: 1.78-1.85 (4H, m), 2.08 (12H, s), 2.11 (12H, s), 2.73-2.79 (4H, m), 3.58 (4H, s), 3.78 (2H, m), 4.51 (2H, m), 7.15-7.26 (10H, m). ^{13}C-NMR δ_C: 19.6, 25.7, 62.1, 65.7, 67.6, 109.0, 127.1, 128.5, 129.0, 142.0, 155.8, 164.6. m.p. decomp > 210°C. m/z(ES) 381.2 (MH^+), 412.2 (OCH_3H^+). HRMS (ESI): MH^+ ($C_{21}H_{28}N_3O_2Al^+$) 381.1997, found 381.2011.

Example 5



10 11

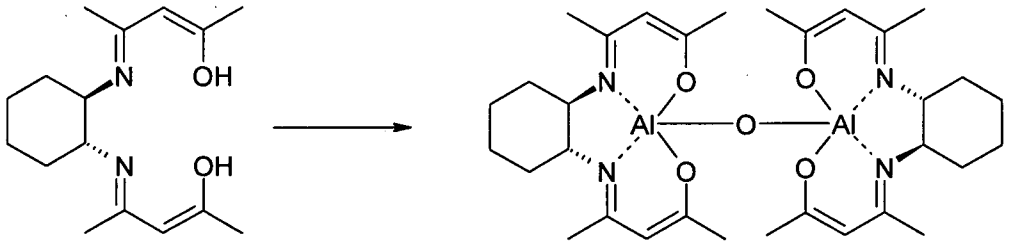
Complex **10** (0.13mmol, 0.1g) was dissolved in acetonitrile (5mL) and benzyl bromide was added (6 eq., 0.8mmol, 0.1mL). The resulting mixture was heated to reflux and stirred for 24 hours during which time a dark orange precipitate formed. After cooling, the solvent was evaporated and the resulting material taken up in ether (*ca.* 20mL) and filtered yielding **11** as a yellow/orange solid.

Example 6

(i) Complex **10** was used as a catalyst in the method of Example 3(i), and had a yield of 6% at 24 hours.

(ii) Complex **11** was used as a catalyst in the method of Example 3(i), except for the absence of the TBAB cocatalyst. The yield was 5% after 24 hours.

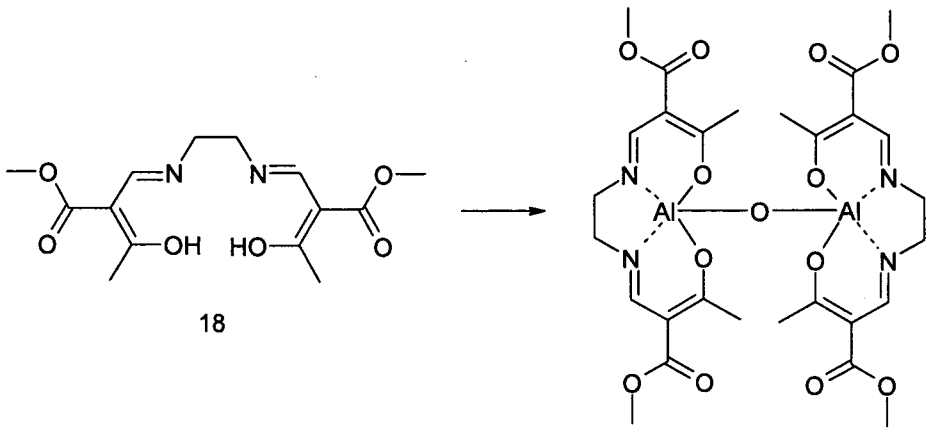
Example 7



14 20

(*R,R*)-Cyclohexanediamine acen ligand (14)(3.0 g, 11.0 mmol) was added to a 5:1 dry toluene / acetonitrile solution (60 mL). Aluminium triethoxide (2.1 g, 13.0 mmol) was then added and the reaction refluxed for 20 hours. The solvent was evaporated *in vacuo* and the residue taken up in dichloromethane (80 mL). The resulting slurry was washed with water (3 x 50 mL) and saturated brine (50 mL). The organic phase was then dried over sodium sulphate, filtered and evaporated *in vacuo*. The residue was rinsed with diethyl ether (*ca.* 30 mL) and dried *in vacuo* for an hour to give the aluminium complex (20) as a pale yellow powder (0.54 g, 0.86 mmol, 16%). Mp >170°C (decomp.), $[\alpha]_D^{23}$ -688 (c = 0.1, MeCN), ν_{max}(ATR) 2931 w, 2859 w, 1606 s and 1577 cm^{-1} s; ^1H NMR ($CDCl_3$): 4.89 (2H, s), 3.1-3.2 (2H, m), 1.98 (6H, s), 1.83 (6H, s), 2.0-1.7 (4H, m), 1.5-1.2 (4H, m).

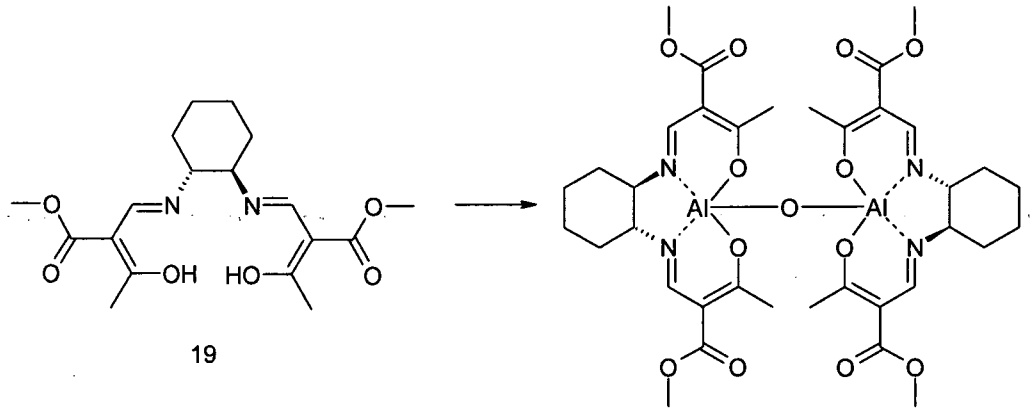
Example 8



18 21

Acen methyl ester ligand (18)(3.0 g, 10.0 mmol) was added to dry toluene and the mixture was heated to reflux to dissolve the ligand. Aluminium triethoxide (1.9g, 12.0 mmol) was added and the reaction refluxed for 20 hours. The solvent was removed *in vacuo*, taken up in dichloromethane (50 mL) and washed with water (3 x 20mL) and brine (20 mL). The organic phase was dried over sodium sulphate and evaporated *in vacuo*. The residue was dried *in vacuo* to give the aluminium complex (21) as a pale yellow powder (3.2 g, 4.6 mmol, 92%). Mp 188-190°C, ν_{max}(ATR) 2949 w, 1695 m and 1616 cm^{-1} s; ^1H NMR ($CDCl_3$): 8.31 (1H, s), 8.09 (1H, s), 3.73 (4H, br, s), 3.69 (6H, s), 2.40 (6H, s); m/z(ESI, MeOH) 705 $(M+Me)^+$, 691 MH^+.

Example 9



19 22

(*R,R*)-Cyclohexanediamine acen methyl ester (19)(3.0 g, 8.2 mmol) was added to dry toluene and the mixture was heated to reflux to dissolve the ligand. Aluminium triethoxide (2.7 g, 16.0 mmol) was added and the reaction refluxed for 22 hours. The solvent was removed *in vacuo* and the residue taken up in dichloromethane (50 mL) and washed with water (3 x 20mL) and brine (20 mL). The organic phase was dried over sodium sulphate and evaporated *in vacuo*. The residue was dried *in vacuo* to give the aluminium complex (22) as a pale yellow powder (2.9 g, 3.6 mmol, 89%). $[\alpha]_D^{23}$ -488 (c = 0.1, MeCN), ^1H NMR ($CDCl_3$): 8.4-7.8 (4H, m), 3.5-3.4 (16H, m), 2.24 (12H, s), 1.9-1.4 (8H, m), 1.2-0.8 (8H, m).

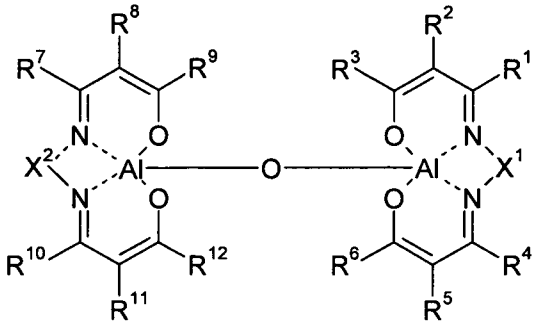
Example 10

Complexes **20**, **21** and **22** were used as a catalyst in the method of Example 3(i), and had yields as shown in the table below:

Catalyst	Conversion %		
	3h	6h	24h
20	2	6	16
21	7	15	36
22	3	6	15

Claims

1. A dimeric aluminium catalyst of formula I:

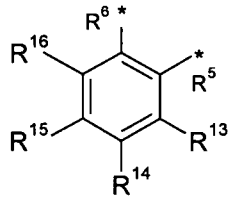


(I)

wherein:

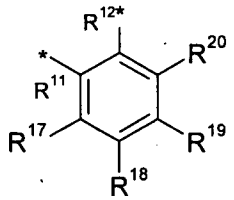
a) each of the substituents R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12}, is independently selected from H, halo, optionally substituted C_{1-20} alkyl, optionally substituted C_{5-20} aryl, optionally substituted C_{3-20} heterocyclyl, ether and nitro, where R^2, R^5, R^8 and R^{11} may additionally be independently selected from optionally substituted ester or optionally substituted acyl or the pairs of R^2 and R^3, R^5 and R^6, R^8 and R^9 and R^{11} and R^{12} may independently together form a C_{2-4} alkylene chain, optionally substituted by one or more groups selected from C_{1-4} alkyl and C_{5-7} aryl; or

b) R^5 and R^6 together with the carbon atoms to which they are attached form an optionally substituted benzene ring of formula:



, and

R^{11} and R^{12} together with the carbon atoms to which they are attached form an optionally substituted benzene ring of formula:



,

each of the substituents R^1, R^2, R^3, R^4, R^7, R^8, R^9, R^{10}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20}, 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 from C_{1-4} alkyl and C_{5-7} aryl or (ii) represent a divalent group selected from C_{5-7} arylene, C_{9-10} arylene, bi-C_{5-7} aryl, bi-C_{9-10} aryl, C_{5-7} cyclic alkylene and C_{3-7} heterocyclylene, which may be optionally substituted.

2. A catalyst according to claim 1, wherein X^1 and X^2 are independently selected from an unsubstituted C_{2-5} alkylene chain and an unsubstituted C_{1-3} bisoxylakylene chain.

3. A catalyst according to claim 1, wherein X^1 and X^2 independently represent C_{5-7} cyclic alkylene.

4. A catalyst according to any one of claims 1 to 3, wherein X^1 and X^2 are the same.

5. A catalyst according to any one of claims 1 to 4, wherein 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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20}, where present, are independently selected, from H, C_{1-7} alkyl, ether and nitro.

6. A catalyst according to any one of claims 1 to 5, wherein $R^1 = R^4 = R^7 = R^{10} =$ H.

7. A catalyst according to any one of claims 1 to 5, wherein $R^1 = R^4 = R^7 = R^{10} =$ Me.

8. A catalyst according to any one of claims 1 to 7, wherein $R^3 = R^6 = R^9 = R^{12} =$ H.

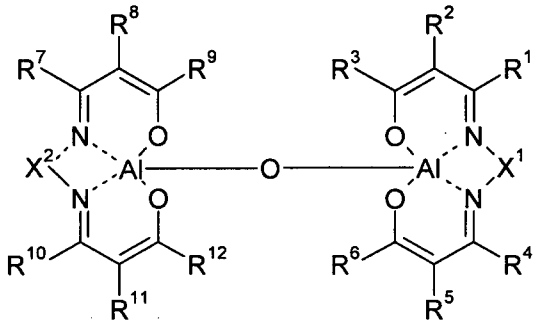
9. A catalyst according to any one of claims 1 to 7, wherein $R^3 = R^6 = R^9 = R^{12} =$ Me.

10. A catalyst according to any one of claims 1 to 9, wherein $R^2 = R^5 = R^8 = R^{11} =$ H.

11. A catalyst according to any one of claims 1 to 10, wherein R^5 and R^6, and R^{11} and R^{12} do not form fused benzene rings.

12. A catalyst according to any one of claims 1 to 11, wherein the catalyst is immobilized on a solid support, either by the use of steric effects or by electrostatic binding.

13. A dimeric aluminium catalyst of formula I:

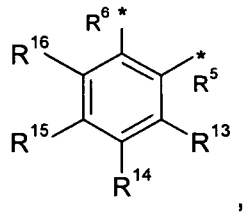


(I)

wherein:

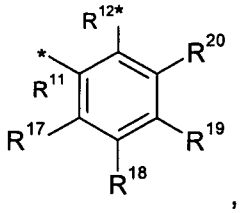
a) each of the substituents R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12}, is independently selected from H, halo, optionally substituted C_{1-20} alkyl, optionally substituted C_{5-20} aryl, optionally substituted C_{3-20} heterocyclyl, ether and nitro, where R^2, R^5, R^8 and R^{11} may additionally be independently selected from optionally substituted ester or optionally substituted acyl or the pairs of R^2 and R^3, R^5 and R^6, R^8 and R^9 and R^{11} and R^{12} may independently together form a C_{2-4} alkylene chain, optionally substituted by one or more groups selected from C_{1-4} alkyl and C_{5-7} aryl; or

b) R^5 and R^6 together with the carbon atoms to which they are attached form an optionally substituted benzene ring of formula:



, and

R^{11} and R^{12} together with the carbon atoms to which they are attached form an optionally substituted benzene ring of formula:



,

each of the substituents R^1, R^2, R^3, R^4, R^7, R^8, R^9, R^{10}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20}, 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_{9-10} arylene, bi-C_{5-7} aryl, bi-C_{9-10} aryl, C_{5-7} cyclic alkylene and C_{3-7} heterocyclylene, which may be optionally substituted, wherein:

(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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) is selected from L-A, where L is a single bond or a C_{1-10} alkylene group and A is an onium 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 forming part of an ammonium group 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)-O-, -C(=O)-NH-, or a single bond; and/or

(d) at least one of R^2, R^5, R^8 and R^{11} is -Q'-L-A, where Q' is either -C(=O)-O- or -C(=O)-;

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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) is L-A', where L is as defined above and A' is an onium 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'; or

(d) one of R^2, R^5, R^8 and R^{11} is -Q'-L-A'.

14. A catalyst according to claim 13, wherein X^1 and X^2 are independently selected from an unsubstituted C_{2-5} alkylene chain and an unsubstituted C_{1-3} bisoxylakylene chain.

15. A catalyst according to either claim 13 or claim 14, wherein X^1 and X^2 are the same.

16. A catalyst according to any one of claims 13 to 15, wherein those 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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) which do not comprise -L-A or -L-A' are independently selected (where appropriate) from H, C_{1-7} alkyl, ether and nitro.

17. A catalyst according to any one of claims 13 to 16, wherein $R^1 = R^4 = R^7 = R^{10} = H$.

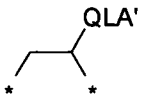
18. A catalyst according to any one of claims 13 to 17, wherein $R^3 = R^6 = R^9 = R^{12} = H$.

19. A catalyst according to any one of claims 13 to 18, wherein R^5 and R^6, and R^{11} and R^{12} do not form fused benzene rings.

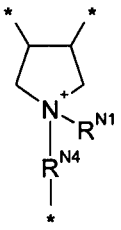
20. A catalyst according to any one of claims 13 to 19, wherein L is an unsubstituted C_{1-3} alkylene group.

21. A catalyst according to any one of claims 13 to 20, 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}, R^{16}, R^{17}, R^{18}, R^{19} and R^{20} (where present) is selected from L-A' and A' is selected from $-NH(CH_3)(CH_2)-$, $-NH(CH(CH_3)_2)(C(CH_3)_2)-$, $-N(CH_3)_2(CH_2)-$, $-N(CH_2CH_3)_2(CH_2CH_2)-$, and $-NHPh(CH_2)-$.

22. A catalyst according to any one of claims 13 to 20, wherein X^1 or X^2 is substituted by -Q-L-A' and is of formula:



23. A catalyst according to any one of claims 13 to 20, 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:

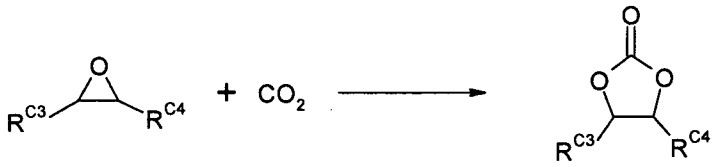


, where R^{N1} is selected from H, C_{1-7} alkyl and C_{5-20} aryl and where R^{N4} is a C_{1-7} alkylene group.

24. A catalyst according to any one of claims 13 to 22, wherein the ammonium counter group is Br^-.

25. A process for the production of cyclic carbonates comprising contacting an epoxide with carbon dioxide in the presence of a catalyst according any one of claims 1 to 12 in combination with a co-catalyst capable of supplying Y^-, where Y is selected from Cl, Br and I; or in the presence of a catalyst according to any one of claims 13 to 24.

26. The process of claim 25, wherein the catalysed reaction is:



II III

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.

27. The process according to claim 26, wherein R^{C4} is H.

28. The process according to either claim 26 or claim 27, wherein R^{C3} is selected from optionally substituted C_{1-4} alkyl and optionally substituted C_{5-7} aryl.

29. The use of a catalyst according any one of claims 1 to 14 in combination with a co-catalyst capable of supplying Y^-, where Y is selected from Cl, Br and I, or a catalyst according to any one of claims 14 to 24 for the production of cyclic carbonates from epoxides.