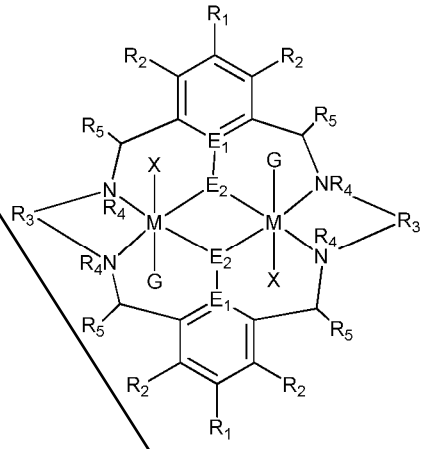
Claims

1. A process for the synthesis of a polycarbonate, the process comprising the step of reacting carbon dioxide with at least one epoxide in the presence of a catalyst of formula (I):



(I)

wherein R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl ether group, or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alicyclic or heteroalicyclic group;

R_3 is independently selected form optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene, may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_4 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

R_5 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

E_1 is C, E_2 is O, S or NH or E_1 is N and E_2 is O;

X is independently selected from $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R_x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

G is absent or independently selected from a neutral or anionic donor ligand which is a Lewis base;

M is independently selected from Zn(II), Cr(II), Co(II), Mn(II), Ti(II), Mg(II), Fe(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Fe(III)-X, Ca(II), Ge(II), Al(III)-X, Ti(III)-X, V(III)-X, Ge(IV)-$(X)_2$ or Ti(IV)-$(X)_2$;

and a chain transfer agent selected from water or a compound of formula (II):

$$Z\text{-}(W)_n \qquad (II)$$

wherein

Z is an optionally substituted moiety selected from the group consisting of aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, polyolefin, polyester, polyether, polycarbonate or combinations thereof,

each W is independently selected from a hydroxyl, amine, thiol or carboxylic acid, and

n is an integer which is at least 1.

2. The process of claim 1, wherein G is independently selected from an optionally substituted heteroaliphatic group, an optionally substituted heteroalicyclic group, an optionally substituted heteroaryl group, a halide, hydroxide, hydride, a carboxylate, an ether, a thioether, carbene, a phosphine, a phosphine oxide, an amine, an acetamide, acetonitrile, an ester, a sulfoxide, a sulfonate and water.

3. The process of claim 1 or 2, wherein the chain transfer agent is water, a mono-alcohol, a diol, a triol, a tetraol, a polyol, a mono-amine, a polyamine, a mono-thiol, a polythiol, a mono-carboxylic acid or a polycarboxylic acid.

4. The process of claim 1, wherein the chain transfer agent is selected from the group consisting of water, diphenylphosphinic acid, 4-ethylbenzenesulfonic acid, methanol, ethanol, propanol, butanol, pentanol, hexanol, phenol, cyclohexanol, 1,2-ethanediol, 1-2-propanediol, 1,3-propanediol, 1,2-butanediol, 1-3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-diphenol, 1,3-diphenol, 1,4-diphenol, catechol,cyclohexenedio), glycerol, benzenetriol, 1,2,4-butanetriol, tris(methylalcohol)propane, tris(methylalcohol)ethane, tris(methylalcohol)nitropropane, D-(+)-glucose, D-sorbitol, calix[4]arene, 2,2-

bis(methylalcohol)-1,3-propanediol, polylactic acid, poly(ethylene glycol), starch, lignin, methylamine, dimethylamine, ethylamine, diethylamine, propylamine, dipropylamine, butylamine, dibutylamine, pentylamine, dipentylamine, hexylamine, dihexylamine, 1,4-butanediamine, 3,5-di-tert-butylbenzoic acid, maleic acid, malonic acid, succinic acid, glutaric acid, terephthalic acid, citric acid, 1,3,5-benzenetricarboxylic acid, 1,3,5-cyclohexanetricarboxylic acid, lactic acid, glycolic acid and 3-hydroxypropionic acid.

5. The process of any preceding claim, wherein the chain transfer agent is present in a molar ratio of at least 1:1 relative to the metal complex.

6. The process of any preceding claim, wherein the chain transfer agent is present in a molar ratio of between about 1:1 and about 100:1 relative to the metal complex.

7. The process of any preceding claim, wherein R_5 is hydrogen.

8. The process of any preceding claim, wherein X is independently selected from $OC(O)R^x$, OSO_2R^x, $OSO(R^x)_2$, OR^x, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl.

9. A polymerisation system for the copolymerisation of carbon dioxide and at least one epoxide comprising:

a) a catalyst of formula (I) as defined in any of claims 1 to 8, and

b) a chain transfer agent of formula (II) as defined in any of claims 1 to 8.

10. A polycarbonate as produced by the process of any of claims 1 to 8.

11. A copolymer of formula B $-(-$ A $)_n$, wherein B is a polycarbonate as produced by the process as defined in any of claims 1 to 8 and each A is a further polymeric unit.

12. The copolymer of claim 11, wherein A is a polymer formed from at least one monomer which is initiated by hydroxyl groups.

13. The copolymer of claims 11 or 12, wherein A is a polymer formed from lactide, lactone, epoxide, cyclic carbonate, epoxide monomers or combinations thereof, or a combination of an epoxide and an anhydride and/or carbon dioxide and/or a di- or poly-carboxylic acid, or a combination of a di-isocyanate and a compound comprising two or more hydroxyl groups (for example a diol, triol, tetraol or polyol).

14. The copolymer of any one of claims 11 to 13, wherein A is a polyester, polyether, polycarbonate, polyamide, polyurethane or any copolymer combination thereof.

15. A method of producing the copolymer of any one of claims 11 to 14, the method comprising the steps of:

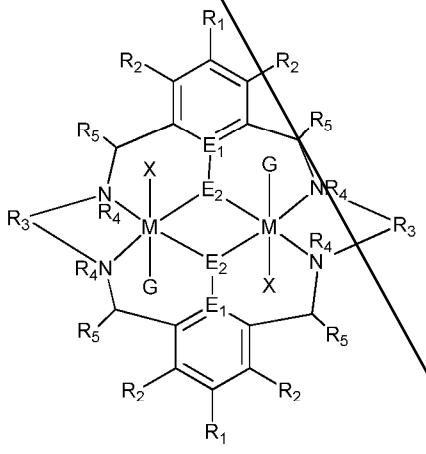
a) synthesising a polycarbonate by the process as defined in any of claims 1 to 8, and

b) ii) - reacting the polycarbonate with at least one further monomer, or

iii) – reacting the polycarbonate with at least one further polymeric unit.

16. The method of claim 15, wherein step b) ii) or iii) occurs *in situ,* directly after step a).

17. A catalyst of formula (III):



(III)

wherein

a) M is independently selected from Mg(II), Ca(II), Ge(II) or Ge(IV)-$(X)_2$,

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an amine, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alicyclic or heteroalicyclic group;

R_3 is independently selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_4 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

R_5 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

E_1 is C, E_2 is O, S or NH or E_1 is N and E_2 is O;

G is absent or independently selected from a neutral or anionic donor ligand which is a Lewis base;

wherein when both instances of G are absent and all instances of R_5 are hydrogen, X is independently selected from $OC(O)R^Z$, $OSO(R^Z)_2$, OSO_2R^Y, $OSOR^T$, OR^V, phosphinate, hydroxyl, carbonate, nitrate or optionally substituted aryl, heteroaryl, alicyclic or heteroalicyclic,

R^Z is independently hydrogen or optionally substituted $C_{2\text{-}20}$aliphatic, $C_{2\text{-}20}$haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R^Y is hydrogen or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl or alkylaryl with the proviso that R^Y is not C_7H_7;

R^V is optionally substituted aryl, haloaryl, heteroaryl, heteroaliphatic, alicyclic, alkylaryl or heteroaliyclic;

R^T is hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

and wherein when either one or both instances of G are not absent, or one or more instances of R_5 is not hydrogen, X is independently selected from $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R_x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R_1, R_2, R_3, R_4, R_5, R^x, R^V, R^Y, R^Z and R^T are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino,

imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or

b) M is independently selected from Zn(II), Co(II), Mn(II), Ti(II), Fe(II), Cr(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Fe(III)-X, Al(III)-X, Ti(III)-X, V(III)-X or Ti(IV)-$(X)_2$,

G is absent or independently selected from a neutral or anionic donor ligand which is a Lewis base;

R_5 is H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

E_1 is C, E_2 is O, S or NH or E_1 is N and E_2 is O; wherein

i) when both instances of G are absent and all instances of R_5 are hydrogen, X is independently selected from $OC(O)R^Z$, $OSO(R^Z)_2$, OSO_2R^Y, $OSOR^T$, OR^V, phosphinate, hydroxyl, carbonate, nitrate or optionally substituted aryl, heteroaryl, alicyclic or heteroalicyclic;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl or alicyclic group;

R_3 is independently selected from optionally substituted alkylene, alkenylene, alkynylene, arylene or cycloalkylene, wherein alkylene, alkenylene or alkynylene may optionally be interrupted by aryl or alicyclic;

R_4 is independently selected from H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

R^Z is independently hydrogen or optionally substituted $C_{2\text{-}20}$aliphatic, $C_{2\text{-}20}$haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R^Y is hydrogen or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl or alkylaryl with the proviso that R^Y is not C_7H_7;

R^V is optionally substituted aryl, haloaryl, heteroaryl, heteroaliphatic, alicyclic, alkylaryl or heteroaliyclic;

R^T is hydrogen, or optionally substituted aliphatic, haloaliphatic, alicyclic, aryl or alkylaryl;

R_1, R_2, R_3 and R_4 are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, imine, nitrile, acetylide, unsubstituted aliphatic, unsubstituted alicyclic and unsubstituted aryl; and

R^V, R^Y, R^Z and R^T are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

ii) when either one or both instances of G are not absent, X is independently selected from $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R^x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl ether group, or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alicyclic or heteroalicyclic;

R_3 is optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_4 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl; and

R_1, R_2, R_3, R_4, R_5 and R^x are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or

iii) when or one or more instances of R_5 are not hydrogen, X is independently selected from $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R^x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl or alicyclic group;

R_3 is independently selected from optionally substituted alkylene, alkenylene, alkynylene, arylene or cycloalkylene, wherein alkylene, alkenylene or alkynylene may optionally be interrupted by aryl or alicyclic;

R_4 is independently selected from H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

R_1, R_2, R_3, R_4 and R_5 are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, imine, nitrile, acetylide, unsubstituted aliphatic, unsubstituted alicyclic and unsubstituted aryl; and

R^x is independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl.

18. The catalyst according to claim 17, wherein M is independently selected from Mg(II), Zn(II), Ca(II), Ge(II), Co(II), Mn(II), Ti(II), Fe(II), Cr(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Fe(III)-X, Al(III)-X, Ti(III)-X, V(III)-X, Ge(IV)-$(X)_2$ or Ti(IV)-$(X)_2$,

G is absent or independently selected from a neutral or anionic donor ligand which is a Lewis base;

R_5 is H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

E_1 is C, E_2 is O, S or NH or E_1 is N and E_2 is O; wherein

i) when both instances of G are absent and all instances of R_5 are hydrogen, X is independently selected from $OC(O)R^Z$, $OSO(R^Z)_2$, OSO_2R^Y, $OSOR^T$, OR^V, phosphinate, hydroxyl, carbonate, nitrate or optionally substituted aryl, heteroaryl, alicyclic or heteroalicyclic;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl or alicyclic group;

R_3 is independently selected from optionally substituted alkylene, alkenylene, alkynylene, arylene or cycloalkylene, wherein alkylene, alkenylene or alkynylene may optionally be interrupted by aryl or alicyclic;

R_4 is independently selected from H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

R^Z is independently hydrogen or optionally substituted C_{2-20}aliphatic, C_{2-20}haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R^Y is hydrogen or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl or alkylaryl with the proviso that R^Y is not C_7H_7;

R^V is optionally substituted aryl, haloaryl, heteroaryl, heteroaliphatic, alicyclic, alkylaryl or heteroaliyclic;

R^T is hydrogen, or optionally substituted aliphatic, haloaliphatic, alicyclic, aryl or alkylaryl;

R_1, R_2, R_3 and R_4 are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, imine, nitrile, acetylide, unsubstituted aliphatic, unsubstituted alicyclic and unsubstituted aryl; and

R^V, $R^{Y,}$ R^Z and R^T are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

ii) when either one or both instances of G are not absent, X is independently selected from $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R^x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl ether group, or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alicyclic or heteroalicyclic;

R_3 is optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_4 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl; and

R_1, R_2, R_3, R_4, R_5 and R^x are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or

iii) when or one or more instances of R_5 are not hydrogen, X is independently selected from $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R^x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl or alicyclic group;

R_3 is independently selected from optionally substituted alkylene, alkenylene, alkynylene, arylene or cycloalkylene, wherein alkylene, alkenylene or alkynylene may optionally be interrupted by aryl or alicyclic;

R_4 is independently selected from H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

R_1, R_2, R_3, R_4 and R_5 are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, imine, nitrile, acetylide, unsubstituted aliphatic, unsubstituted alicyclic and unsubstituted aryl; and

R^x is independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl.

19. The catalyst according to claim 17 or 18, wherein M is independently selected from Mg(II), Zn(II), Ca(II), Ge(II), Co(II), Mn(II), Ti(II), Fe(II), Cr(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Fe(III)-X, Al(III)-X, Ti(III)-X, V(III)-X, Ge(IV)-$(X)_2$ or Ti(IV)-$(X)_2$,

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl or alicyclic group;

R_3 is independently selected from optionally substituted alkylene, alkenylene, alkynylene, arylene or cycloalkylene, wherein alkylene, alkenylene or alkynylene may optionally be interrupted by aryl or alicyclic;

R_4 is independently selected from H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

R_5 is H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

E_1 is C, E_2 is O, S or NH or E_1 is N and E_2 is O;

G is absent or independently selected from a neutral or anionic donor ligand which is a Lewis base;

X is independently selected from $OC(O)R^Z$, $OSO(R^Z)_2$, OSO_2R^Y, $OSOR^T$, OR^V, phosphinate, hydroxyl, carbonate, nitrate or optionally substituted aryl, heteroaryl, alicyclic or heteroalicyclic;

R^Z is independently hydrogen or optionally substituted C_{2-20}aliphatic, C_{2-20}haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R^Y is hydrogen or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl or alkylaryl with the proviso that R^Y is not C_7H_7;

R^V is optionally substituted aryl, haloaryl, heteroaryl, heteroaliphatic, alicyclic, alkylaryl or heteroaliyclic;

R^T is hydrogen, or optionally substituted aliphatic, haloaliphatic, alicyclic, aryl or alkylaryl;

R_1, R_2, R_3, R_4 and R_5 are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, imine, nitrile, acetylide, unsubstituted aliphatic, unsubstituted alicyclic and unsubstituted aryl; and

R^V, R^Y, R^Z and R^T are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl.

20. The catalyst according to claim 17 or 18, wherein the catalyst is:

$[L^1Mg_2Cl_2(methylimidazole)]$,

$[L_1Mg_2Cl_2(dimethylaminopyridine)]$,

$[L_1Mg_2Br_2(dimethylaminopyridine)]$,

$[L^1Zn_2(OOCC(CH_3)_3)_2]$,

$[L^1Zn_2(pentafluorobenzoate)_2]$,

$[L^1Zn_2(adamantyl\ carboxylate)_2]$,

$[L^1Zn_2(diphenyl\ phosphinate)_2]$,

$[L^1Zn_2(bis(4\text{-}methoxy)phenyl\ phosphinate)_2]$,

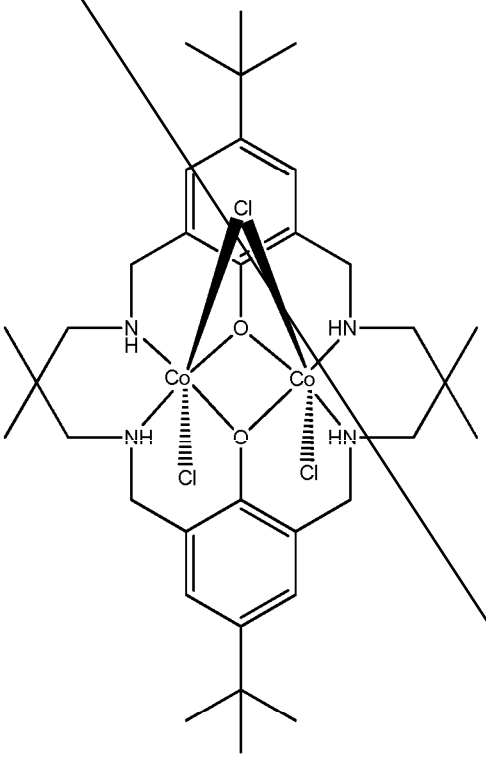
$[L^4Mg_2(OCOCH_3)_2]$,

$[L^1Zn_2(OC_6H_5)_2]$,

$[L^1Zn_2(hexanoate)_2]$,

$[L^1Zn_2(octanoate)_2]$,

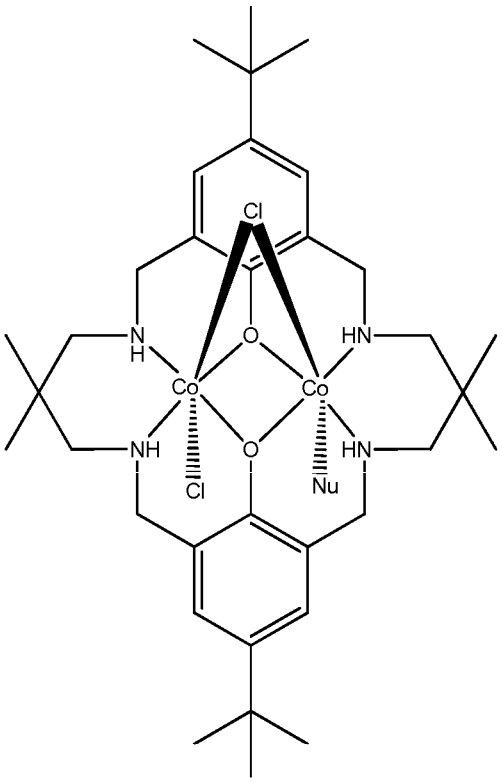
$[L^1Zn_2(dodecanoate)_2]$, and



$[L^1Co_2Cl_3]^-[B\text{-}H]^+$

$[B\text{-}H]^+$ represents any counterion, for example,
B may be NEt_3, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),
7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), etc

or



$[L^1Co_2Cl_2Nu]$

Nu = N-methylimidazole
= pyridine
= dimethylaminopyridine

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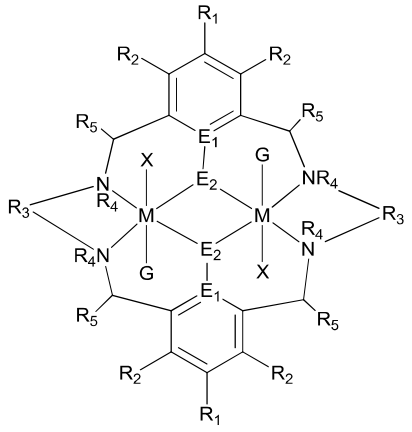
Claims

1. A process for the synthesis of a polycarbonate, the process comprising the step of reacting carbon dioxide with at least one epoxide in the presence of a catalyst of formula (I):



(I)

wherein:

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl ether group, or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alicyclic or heteroalicyclic group;

R_3 is independently optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene, may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_4 is independently H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

R_5 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

E_1 is C and E_2 is O, S or NH; or E_1 is N and E_2 is O;

X is independently $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R_x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

G is absent or independently a neutral or anionic donor ligand which is a Lewis base; and

M is independently Zn(II), Cr(II), Co(II), Mn(II), Ti(II), Mg(II), Fe(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Fe(III)-X, Ca(II), Ge(II), Al(III)-X, Ti(III)-X, V(III)-X, Ge(IV)-$(X)_2$ or Ti(IV)-$(X)_2$;

and a chain transfer agent, wherein the chain transfer agent is water or a compound of formula (II):

$$Z-(W)_n \qquad \text{(II)}$$

wherein:

Z is an optionally substituted moiety selected from the group consisting of aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, polyolefin, polyester, polyether, polycarbonate and combinations thereof;

each W is independently a hydroxyl, amine, thiol or carboxylic acid; and

n is an integer which is at least 1;

wherein the chain transfer agent is present in a molar ratio of at least 1:1 relative to the catalyst of formula (I).

2. The process of claim 1, wherein G is independently an optionally substituted heteroaliphatic group, an optionally substituted heteroalicyclic group, an optionally substituted heteroaryl group, a halide, hydroxide, hydride, a carboxylate, an ether, a thioether, carbene, a phosphine, a phosphine oxide, an amine, an acetamide, acetonitrile, an ester, a sulfoxide, a sulfonate or water.

3. The process of claim 1, wherein the chain transfer agent is water, a mono-alcohol, a diol, a triol, a tetraol, a polyol, a mono-amine, a polyamine, a mono-thiol, a polythiol, a mono-carboxylic acid or a polycarboxylic acid.

4. The process of claim 1, wherein the chain transfer agent is selected from the group consisting of water, diphenylphosphinic acid, 4-ethylbenzenesulfonic acid, methanol, ethanol, propanol, butanol, pentanol, hexanol, phenol, cyclohexanol, 1,2-ethanediol, 1-2-propanediol, 1,3-propanediol, 1,2-butanediol, 1-3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-diphenol, 1,3-diphenol, 1,4-diphenol, catechol, cyclohexanediol, glycerol, benzenetriol, 1,2,4-butanetriol, tris(methylalcohol)propane, tris(methylalcohol)ethane, tris(methylalcohol)nitropropane, D-(+)-glucose, D-sorbitol, calix[4]arene, 2,2-bis(methylalcohol)-1,3-propanediol, polylactic acid, poly(ethylene glycol), starch, lignin, methylamine, dimethylamine, ethylamine, diethylamine, propylamine, dipropylamine, butylamine, dibutylamine, pentylamine, dipentylamine, hexylamine, dihexylamine, 1,4-butanediamine, 3,5-di-tert-butylbenzoic acid, maleic acid, malonic acid, succinic acid, glutaric acid, terephthalic acid, citric acid, 1,3,5-benzenetricarboxylic acid, 1,3,5-cyclohexanetricarboxylic acid, lactic acid, glycolic acid and 3-hydroxypropionic acid.

5. The process of claim 1, wherein the chain transfer agent is present in a molar ratio of between about 1:1 and about 100:1 relative to the metal complex.

6. The process of claim 1, wherein R_5 is hydrogen.

7. The process of claim 1, wherein X is independently $OC(O)R^x$, OSO_2R^x, $OSO(R^x)_2$, OR^x, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl.

8. A polymerisation system for the copolymerisation of carbon dioxide and at least one epoxide comprising:

a) a catalyst of formula (I) as defined in claim 1, and

b) a chain transfer agent of formula (II) as defined in claim 1.

9. A method of producing the copolymer of formula B –(A)$_n$, wherein B is a polycarbonate as produced by the process as defined in claim 1, and each A is a further polymeric unit, the method comprising the steps of:

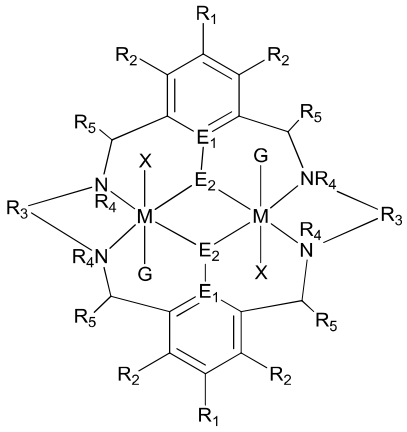
a) synthesising a polycarbonate by the process as defined in claim 1, and

b) ii) – reacting the polycarbonate with at least one further monomer, or

iii) – reacting the polycarbonate with at least one further polymeric unit.

10. The method of claim 9, wherein step b) ii) or iii) occurs *in situ,* directly after step a).

11. A catalyst of formula (III):



(III)

wherein

a) M is independently Mg(II), Ca(II), Ge(II) or Ge(IV)-(X)$_2$,

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an amine, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alicyclic or heteroalicyclic group;

R_3 is independently optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_4 is independently H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

R_5 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

E_1 is C, and E_2 is O, S or NH; or E_1 is N and E_2 is O;

G is absent or independently a neutral or anionic donor ligand which is a Lewis base;

wherein when both instances of G are absent and all instances of R_5 are hydrogen, X is independently $OC(O)R^Z$, $OSO(R^Z)_2$, OSO_2R^Y, $OSOR^T$, OR^V, phosphinate, hydroxyl, carbonate, nitrate or optionally substituted aryl, heteroaryl, alicyclic or heteroalicyclic,

R^Z is independently hydrogen or optionally substituted $C_{2\text{-}20}$aliphatic, $C_{2\text{-}20}$haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R^Y is hydrogen or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl or alkylaryl with the proviso that R^Y is not C_7H_7;

R^V is optionally substituted aryl, haloaryl, heteroaryl, heteroaliphatic, alicyclic, alkylaryl or heteroaliyclic;

R^T is hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

and wherein when either one or both instances of G are not absent, or one or more instances of R_5 is not hydrogen, X is independently $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R_x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R_1, R_2, R_3, R_4, R_5, R^x, R^V, R^Y, R^Z and R^T are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or

b) M is independently Zn(II), Co(II), Mn(II), Ti(II), Fe(II), Cr(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Fe(III)-X, Al(III)-X, Ti(III)-X, V(III)-X or Ti(IV)-$(X)_2$,

G is absent or independently a neutral or anionic donor ligand which is a Lewis base;

R_5 is H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

E_1 is C and E_2 is O, S or NH; or E_1 is N and E_2 is O; wherein

i) when both instances of G are absent and all instances of R_5 are hydrogen, X is independently $OC(O)R^Z$, $OSO(R^Z)_2$, OSO_2R^Y, $OSOR^T$, OR^V, phosphinate, hydroxyl, carbonate, nitrate or optionally substituted aryl, heteroaryl, alicyclic or heteroalicyclic;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl or alicyclic group;

R_3 is independently optionally substituted alkylene, alkenylene, alkynylene, arylene or cycloalkylene, wherein alkylene, alkenylene or alkynylene may optionally be interrupted by aryl or alicyclic;

R_4 is independently H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

R^Z is independently hydrogen or optionally substituted $C_{2\text{-}20}$aliphatic, $C_{2\text{-}20}$haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R^Y is hydrogen or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl or alkylaryl with the proviso that R^Y is not C_7H_7;

R^V is optionally substituted aryl, haloaryl, heteroaryl, heteroaliphatic, alicyclic, alkylaryl or heteroaliyclic;

R^T is hydrogen, or optionally substituted aliphatic, haloaliphatic, alicyclic, aryl or alkylaryl;

R_1, R_2, R_3 and R_4 are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, imine, nitrile, acetylide, unsubstituted aliphatic, unsubstituted alicyclic or unsubstituted aryl; and

R^V, R^Y, R^Z and R^T are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

ii) when either one or both instances of G are not absent, X is independently $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R^x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl ether group, or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alicyclic or heteroalicyclic;

R_3 is optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_4 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl; and

R_1, R_2, R_3, R_4, R_5 and R^x are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or

iii) when or one or more instances of R_5 are not hydrogen, X is independently $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R^x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl or alicyclic group;

R_3 is independently optionally substituted alkylene, alkenylene, alkynylene, arylene or cycloalkylene, wherein alkylene, alkenylene or alkynylene may optionally be interrupted by aryl or alicyclic;

R_4 is independently H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

R_1, R_2, R_3, R_4 and R_5 are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, imine, nitrile, acetylide, unsubstituted aliphatic, unsubstituted alicyclic or unsubstituted aryl; and

R^x is independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

with the proviso that the catalyst is not:

$[Co_2LCl_2(CH_3OH)_2] \cdot H_2O$,

$[Co_2LBr_2(CH_3OH)_2] \cdot H_2O$,

$[Mn_2LCl_2(CH_3OH)_2] \cdot H_2O$,

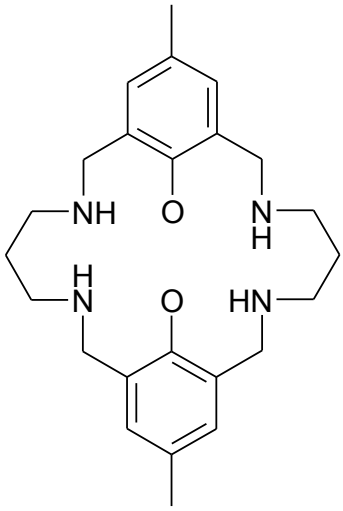
$[Mn_2LBr_2(CH_3OH)_2] \cdot H_2O$,

$[Co^{II}Co^{III}LCl_2Br(CH_3OH)] \cdot 0.5CH_2Cl_2$,

$[Mn^{II}Mn^{III}LCl_2Br(CH_3OH)]$, or

$[Fe^{II}Co^{II}L(\mu\text{-}OAc)(OAc)(H_2O)]$,

wherein L is



L .

12. The catalyst according to claim 11, wherein M is independently Mg(II), Zn(II), Ca(II), Ge(II), Co(II), Mn(II), Ti(II), Fe(II), Cr(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Fe(III)-X, Al(III)-X, Ti(III)-X, V(III)-X, Ge(IV)-$(X)_2$ or Ti(IV)-$(X)_2$,

G is absent or independently a neutral or anionic donor ligand which is a Lewis base;

R_5 is H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

E_1 is C and E_2 is O, S or NH; or E_1 is N and E_2 is O; wherein

i) when both instances of G are absent and all instances of R_5 are hydrogen, X is independently $OC(O)R^Z$, $OSO(R^Z)_2$, OSO_2R^Y, $OSOR^T$, OR^V, phosphinate, hydroxyl, carbonate, nitrate or optionally substituted aryl, heteroaryl, alicyclic or heteroalicyclic;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl or alicyclic group;

R_3 is independently optionally substituted alkylene, alkenylene, alkynylene, arylene or cycloalkylene, wherein alkylene, alkenylene or alkynylene may optionally be interrupted by aryl or alicyclic;

R_4 is independently H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

R^Z is independently hydrogen or optionally substituted $C_{2\text{-}20}$aliphatic, $C_{2\text{-}20}$haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R^Y is hydrogen or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl or alkylaryl with the proviso that R^Y is not C_7H_7;

R^V is optionally substituted aryl, haloaryl, heteroaryl, heteroaliphatic, alicyclic, alkylaryl or heteroaliyclic;

R^T is hydrogen, or optionally substituted aliphatic, haloaliphatic, alicyclic, aryl or alkylaryl;

R_1, R_2, R_3 and R_4 are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, imine, nitrile, acetylide, unsubstituted aliphatic, unsubstituted alicyclic and unsubstituted aryl; and

R^V, R^Y, R^Z and R^T are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

ii) when either one or both instances of G are not absent, X is independently $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R^x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl ether group, or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alicyclic or heteroalicyclic;

R_3 is optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_4 is H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl; and

R_1, R_2, R_3, R_4, R_5 and R^x are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl; or

iii) when or one or more instances of R_5 are not hydrogen, X is independently $OC(O)R^x$, OSO_2R^x, $OSOR^x$, $OSO(R^x)_2$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

R^x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl or alicyclic group;

R_3 is independently optionally substituted alkylene, alkenylene, alkynylene, arylene or cycloalkylene, wherein alkylene, alkenylene or alkynylene may optionally be interrupted by aryl or alicyclic;

R_4 is independently H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

R_1, R_2, R_3, R_4 and R_5 are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, imine, nitrile, acetylide, unsubstituted aliphatic, unsubstituted alicyclic or unsubstituted aryl; and

R^x is independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl.

13. The catalyst according to claim 11, wherein M is independently Mg(II), Zn(II), Ca(II), Ge(II), Co(II), Mn(II), Ti(II), Fe(II), Cr(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Fe(III)-X, Al(III)-X, Ti(III)-X, V(III)-X, Ge(IV)-$(X)_2$ or Ti(IV)-$(X)_2$,

R_1 and R_2 are independently hydrogen, halide, a nitro group, a nitrile group, an imine, an ether group, a silyl ether group or an acetylide group or optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl or alicyclic group;

R_3 is independently optionally substituted alkylene, alkenylene, alkynylene, arylene or cycloalkylene, wherein alkylene, alkenylene or alkynylene may optionally be interrupted by aryl or alicyclic;

R_4 is independently H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

R_5 is H, or optionally substituted aliphatic, alicyclic, aryl, or alkylaryl;

E_1 is C and E_2 is O, S or NH; or E_1 is N and E_2 is O;

G is absent or independently a neutral or anionic donor ligand which is a Lewis base;

X is independently $OC(O)R^Z$, $OSO(R^Z)_2$, OSO_2R^Y, $OSOR^T$, OR^V, phosphinate, hydroxyl, carbonate, nitrate or optionally substituted aryl, heteroaryl, alicyclic or heteroalicyclic;

R^Z is independently hydrogen or optionally substituted $C_{2\text{-}20}$aliphatic, $C_{2\text{-}20}$haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl;

R^Y is hydrogen or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl or alkylaryl with the proviso that R^Y is not C_7H_7;

R^V is optionally substituted aryl, haloaryl, heteroaryl, heteroaliphatic, alicyclic, alkylaryl or heteroaliyclic;

R^T is hydrogen, or optionally substituted aliphatic, haloaliphatic, alicyclic, aryl or alkylaryl;

R_1, R_2, R_3, R_4 and R_5 are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, imine, nitrile, acetylide, unsubstituted aliphatic, unsubstituted alicyclic or unsubstituted aryl; and

R^V, R^Y, R^Z and R^T are each independently optionally substituted by halogen, hydroxyl, nitro, carbonate, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, or unsubstituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl.

14. The catalyst according to claim 11, wherein the catalyst is:

$[L^1Mg_2Cl_2(methylimidazole)]$,

$[L_1Mg_2Cl_2(dimethylaminopyridine)]$,

$[L_1Mg_2Br_2(dimethylaminopyridine)]$,

$[L^1Zn_2(OOCC(CH_3)_3)_2]$,

$[L^1Zn_2(pentafluorobenzoate)_2]$,

$[L^1Zn_2(adamantyl\ carboxylate)_2]$,

$[L^1Zn_2(diphenyl\ phosphinate)_2]$,

$[L^1Zn_2(bis(4\text{-}methoxy)phenyl\ phosphinate)_2]$,

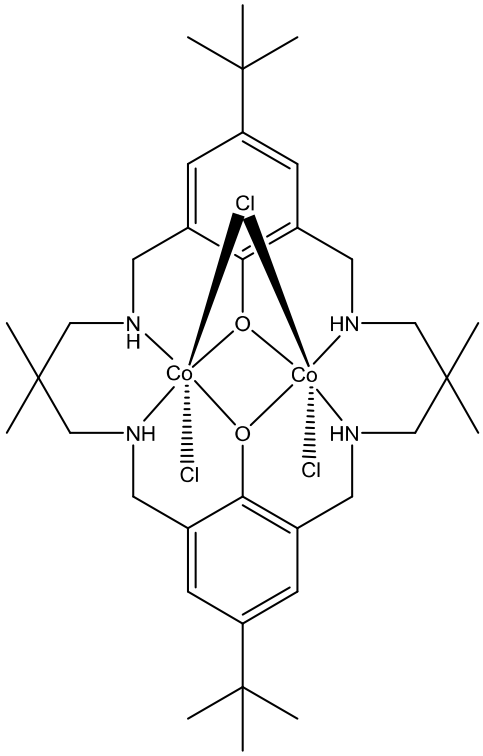
$[L^4Mg_2(OCOCH_3)_2]$,

$[L^1Zn_2(OC_6H_5)_2]$,

$[L^1Zn_2(hexanoate)_2]$,

$[L^1Zn_2(octanoate)_2]$,

$[L^1Zn_2(dodecanoate)_2]$,



$[L^1Co_2Cl_3]^-$ $[B\text{-}H]^+$

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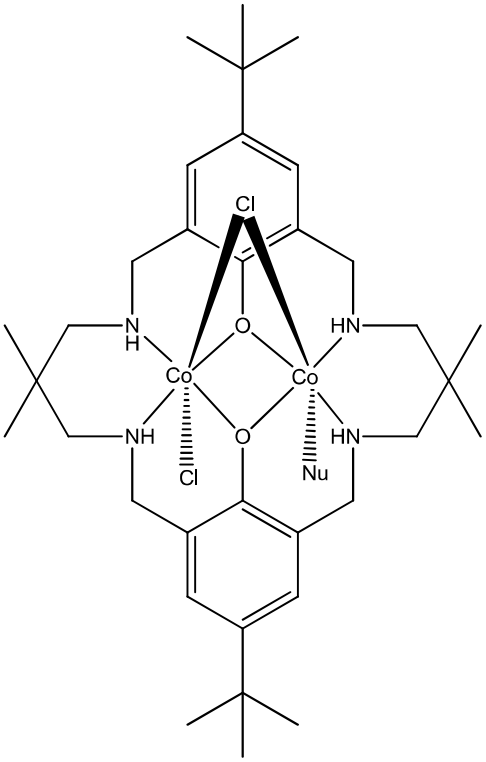
wherein $[B\text{-}H]^+$ represents any counterion, or



$[L^1Co_2Cl_2Nu]$

wherein Nu is N-methylimidazole, pyridine, or dimethylaminopyridine.

15. The method of claim 9, wherein A is a polymer formed from at least one monomer which is initiated by hydroxyl groups.

16. The method of claim 9, wherein A is a polymer formed from lactide, lactone, epoxide, cyclic carbonate, epoxide monomers or combinations thereof, or a combination of an epoxide and an anhydride and/or carbon dioxide and/or a di- or poly-carboxylic acid, or a combination of a di-isocyanate and a compound comprising two or more hydroxyl groups, or wherein A is a polyester, polyether, polycarbonate, polyamide, polyurethane or any copolymer combination thereof.

17. The process of claim 1, wherein the chain transfer agent is present in a molar ratio of at least about 2:1 relative to the catalyst of formula (I).

18. The process of claim 1, wherein the chain transfer agent is present in a molar ratio of at least about 4:1 relative to the catalyst of formula (I).

19. The process of claim 1, wherein the chain transfer agent is present in a molar ratio of at least about 8:1 relative to the catalyst of formula (I).