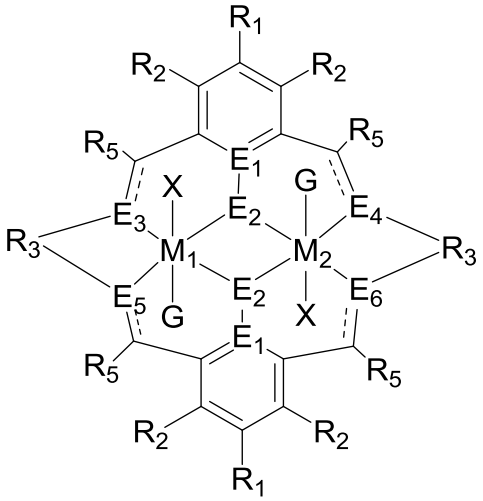
Claims

1. A method for preparing a polycarbonate ether polyol, the method comprising reacting carbon dioxide and an epoxide in the presence of a double metal cyanide (DMC) catalyst, a catalyst of formula (I), and a starter compound,
wherein the catalyst of formula (I) has the following structure:



(I)

Wherein M_1 and M_2 are independently selected from Zn(II), Cr(II), Co(II), Cu(II), Mn(II), Mg(II), Ni(II), Fe(II), Ti(II), V(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Ni(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)-$(X)_2$;
R_1 and R_2 are independently selected from hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl group, a silyl ether group, a sulfoxide group, a sulfonyl group, a sulfinate group or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alkoxy, aryloxy, alkylthio, arylthio, 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_5 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;
E_1 is C and E_2 is O;
E_3, E_4, E_5 and E_6 are selected from N, NR_4, O and S, wherein when E_3, E_4, E_5 or E_6 are N, ------ is ═══, and wherein when E_3, E_4, E_5 or E_6 are NR_4, O or S, ------ is ———;

R_4 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl, -alkylC(O)OR_{19} or -alkylC≡N or alkylaryl;

X is independently selected from $OC(O)R_x$, OSO_2R_x, $OSOR_x$, $OSO(R_x)_2$, $S(O)R_x$, OR_x, phosphinate, halide, nitrate, hydroxyl, carbonate, amino, 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; and

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

and wherein the starter is a compound having the following structure:

$$Z\text{-}(R^Z)_a \qquad \text{(III)}$$

Z is selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, cycloalkylene, cycloalkenylene, hererocycloalkylene, heterocycloalkenylene, arylene, heteroarylene, or Z may be a combination of any of these groups, such as an alkylarylene, heteroalkylarylene, heteroalkylheteroarylene or alkylheteroarylene group;

a is an integer which is at least 2; and

each R^Z may be –OH, -NHR', –SH, -C(O)OH, PR'(O)$(OH)_2$, -P(O)(OR')(OH) or –PR'(O)OH, preferably R^z may be –OH, -C(O)OH or –NHR', more preferably each R^Z may be –OH, -C(O)OH or a combination thereof.

2. The method of claim 1 wherein the reaction is carried out at a pressure of between about 1 bar and about 60 bar carbon dioxide, preferably between about 1 bar and about 30 bar carbon dioxide, more preferably between about 1 bar and about 20 bar carbon dioxide, more preferably between about 1 bar and about 15 bar carbon dioxide, more preferably between about 1 bar and about 10 bar carbon dioxide.

3. The method of claim 1 or 2, wherein M_1 and/or M_2 is selected from Mg(II), Zn(II), or Ni(II), preferably wherein M_1 and M_2 are selected from Mg(II), Zn(II), or Ni(II),.

4. The method of any preceding claim, wherein X is independently selected from $OC(O)R^x$, OSO_2R^x, $OS(O)R^x$, $OSO(R^x)_2$, $S(O)R^x$, OR^x, halide, nitrate, hydroxyl, carbonate, amino, nitro, amido, alkyl, heteroalkyl, aryl or heteroaryl, and/or R^x may be optionally substituted alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl,

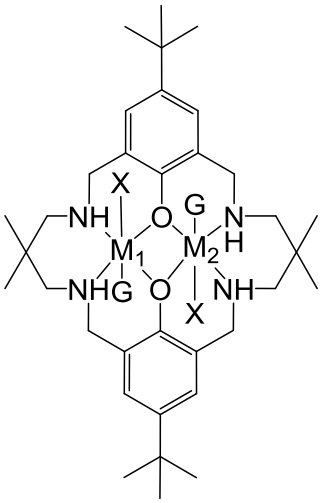
cycloalkyl, or alkylaryl.

5. The method of any preceding claim, wherein the catalyst of formula (I) has a symmetric macrocyclic ligand.

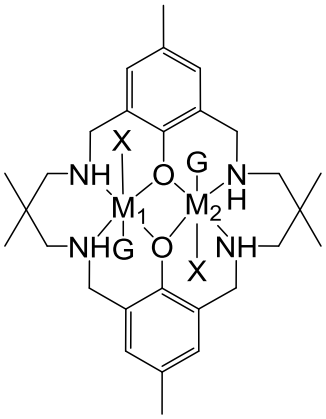
6. The method of any of claims 1 to 4, wherein the catalyst of formula (I) has an asymmetric macrocyclic ligand.

7. The method of claim 6, wherein E_3, E_4, E_5 and E_6 are NR_4, wherein at least one occurrence of E_3, E_4, E_5 and E_6 is different to the remaining occurrence(s) of E_3, E_4, E_5 and E_6 are, preferably wherein R_4 is H or alkyl.

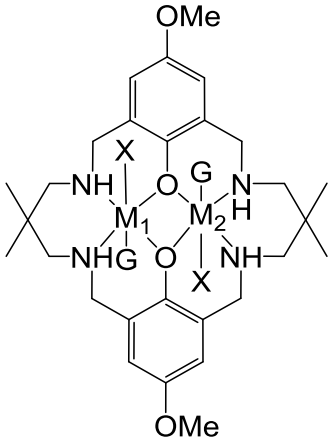
8. The method according to any preceding claim, wherein the catalyst is of the formula:



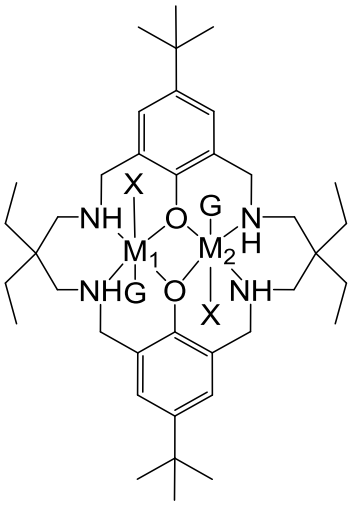
$[L^1M_1M_2(X)_2(G)_2]$



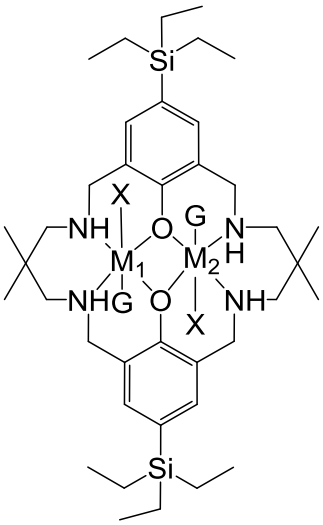
$[L^2M_1M_2(X)_2(G)_2]$



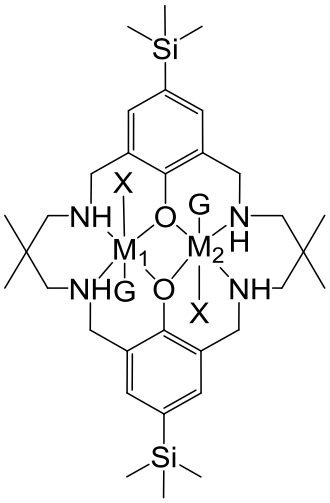
$[L^3M_1M_2(X)_2(G)_2]$



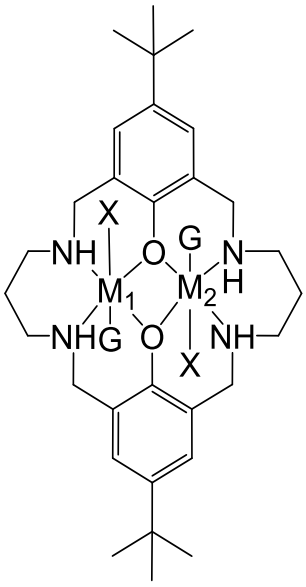
$[L^4M_1M_2(X)_2(G)_2]$



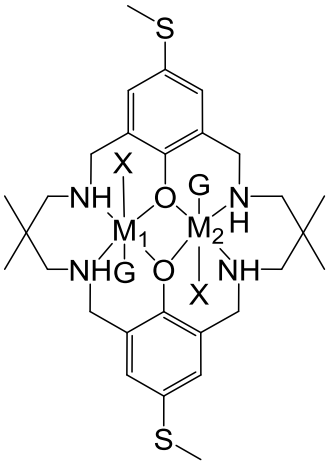
$[L^5M_1M_2(X)_2(G)_2]$



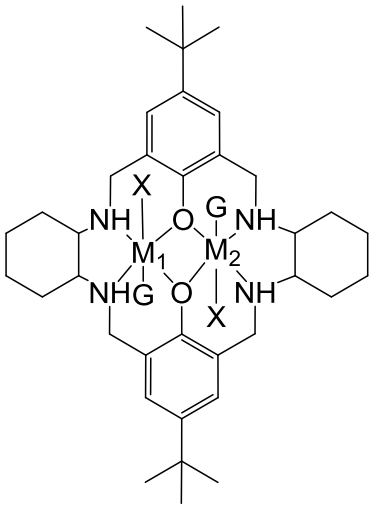
$[L^6M_1M_2(X)_2(G)_2]$



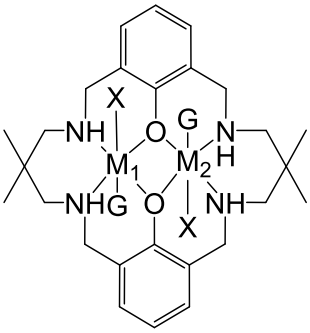
$[L^{7}M_1M_2(X)_2(G)_2]$



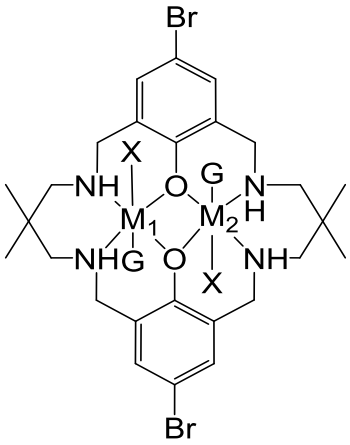
$[L^{8}M_1M_2(X)_2(G)_2]$



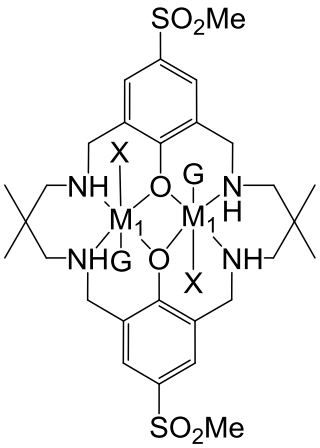
$[L^{9}M_1M_2(X)_2(G)_2]$



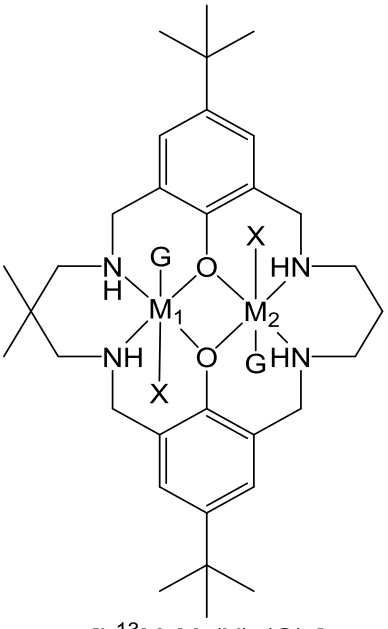
$[L^{10}M_1M_2(X)_2(G)_2]$



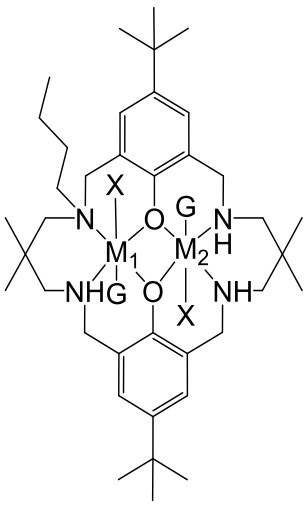
$[L^{11}M_1M_2(X)_2(G)_2]$



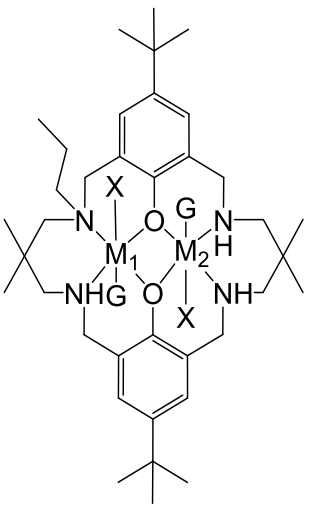
$[L^{12}M_1M_2(X)_2(G)_2]$



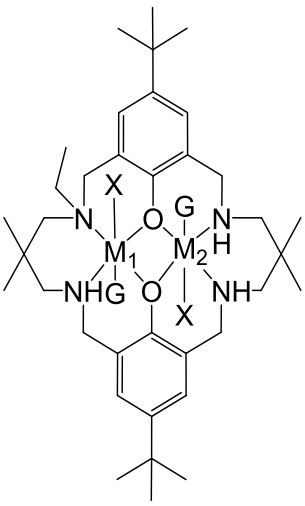
$[L^{13}M_1M_2(X)_2(G)_2]$



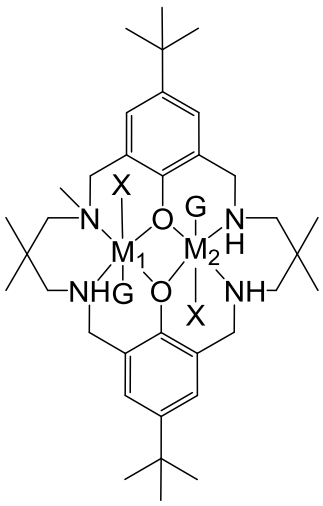
$[L^{14}M_1M_2(X)_2(G)_2]$



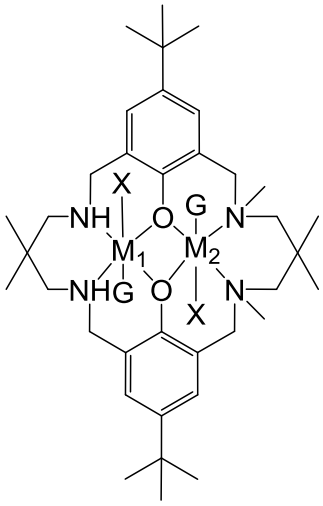
$[L^{15}M_1M_2(X)_2(G)_2]$



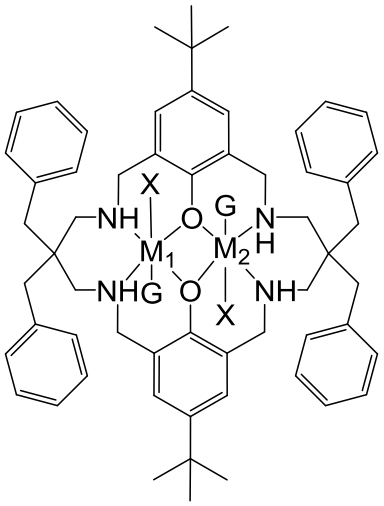
$[L^{16}M_1M_2(X)_2(G)_2]$



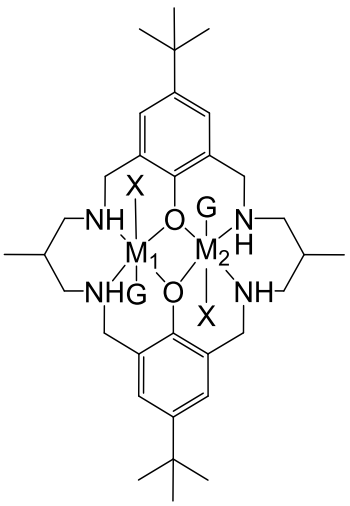
$[L^{17}M_1M_2(X)_2(G)_2]$



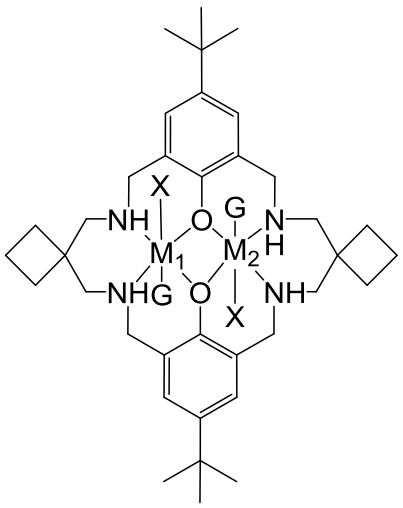
$[L^{18}M_1M_2(X)_2(G)_2]$



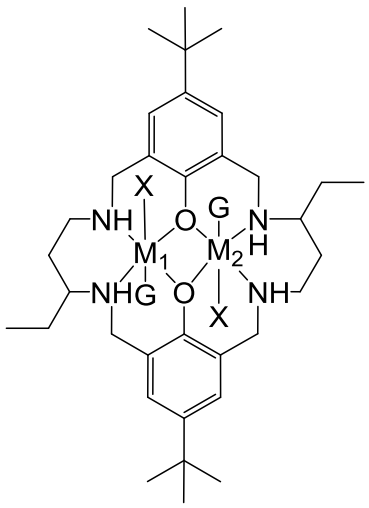
$[L^{19}M_1M_2(X)_2(G)_2]$



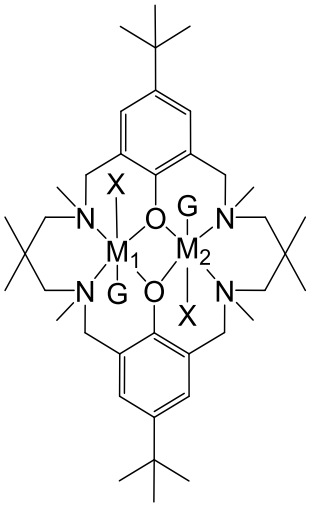
$[L^{20}M_1M_2(X)_2(G)_2]$



$[L^{21}M_1M_2(X)_2(G)_2]$ or $[L^{22}M_1M_2(X)_2(G)_2]$.



9. The method according to any of claims 1 to 7, wherein the catalyst is of the formula:



$[L^{23}M_1M_2(X)_2(G)_2]$.

10. The method of any preceding claim, wherein the reaction is carried out at a temperature in the range of from about 50˚C to about 110˚C, preferably from about 60°C to about 100°C.

11. The method of any preceding claim, wherein each occurrence of R^Z may be –OH.

12. The method of any preceding claim, wherein a is an integer in the range of between about 2 and about 8, preferably in the range of about 2 and about 6.

13. The method of any of claims 1 to 10, wherein the starter compound is from diols such as 1,2-ethanediol (ethylene glycol), 1-2-propanediol, 1,3-propanediol (propylene glycol), 1,2-butanediol, 1-3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,4-cyclohexanediol, 1,2-diphenol, 1,3-diphenol, 1,4-diphenol, neopentyl glycol, catechol, cyclohexenediol, 1,4-cyclohexanedimethanol, dipropylene glycol, diethylene glycol, tripropylene glycol, triethylene glycol, tetraethylene glycol, polypropylene glycols (PPGs) or polyethylene glycols (PEGs) having an Mn of up to about 1500g/mol, such as PPG 425, PPG 725, PPG 1000 and the like, triols such as glycerol, benzenetriol, 1,2,4-butanetriol, 1,2,6-hexanetriol, tris(methylalcohol)propane, tris(methylalcohol)ethane, tris(methylalcohol)nitropropane, trimethylol propane, polypropylene oxide triols and polyester triols, tetraols such as calix[4]arene, 2,2-bis(methylalcohol)-1,3-propanediol, erythritol, pentaerythritol or polyalkylene glycols (PEGs or PPGs) having 4–OH groups, polyols, such as sorbitol or polyalkylene glycols (PEGs or PPGs) having 5 or more –OH groups, diacids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid,

suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid or other compounds having mixed functional groups such as lactic acid, glycolic acid, 3-hydroxypropanoic acid, 4-hydroxybutanoic acid, 5-hydroxypentanoic acid.

14. The method of any of claims 1 to 10, wherein the starter compound is a diol such as 1,2-ethanediol (ethylene glycol), 1-2-propanediol, 1,3-propanediol (propylene glycol), 1,2-butanediol, 1-3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-dodecanediol, 1,4-cyclohexanediol, 1,2-diphenol, 1,3-diphenol, 1,4-diphenol, neopentyl glycol, catechol, cyclohexenediol, 1,4-cyclohexanedimethanol, poly(caprolactone) diol, dipropylene glycol, diethylene glycol, tripropylene glycol, triethylene glycol, tetraethylene glycol, polypropylene glycols (PPGs) or polyethylene glycols (PEGs) having an Mn of up to about 1500g/mol, such as PPG 425, PPG 725, PPG 1000 and the like, preferably wherein the starter compound is 1,6-hexanediol, 1,4-cyclohexanedimethanol, 1,12-dodecanediol, poly(caprolactone) diol, PPG 425, PPG 725, or PPG 1000.

15. The method of any preceding claim, wherein the DMC catalyst is prepared by treating an aqueous solution of a metal salt with an aqueous solution of a metal cyanide salt in the presence of an organic complexing agent, preferably wherein the metal salt is of the formula $M'(X')_p$, wherein M' is selected from Zn(II), Fe(II), Ni(II), Mn(II), Co(II), Sn(II), Pb(II), Fe(III), Mo(IV), Mo(VI), Al(III), V(V), V(VI), Sr(II), W(IV), W(VI), Cu(II), and Cr(III),
X' is an anion selected from halide, hydroxide, sulphate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate and nitrate,
p is an integer of 1 or more, and the charge on the anion multiplied by p satisfies the valency of M';
the metal cyanide salt is of the formula $(Y)_qM''(CN)_b(A)_c$, wherein M'' is selected from Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), Ir(III), Ni(II), Rh(III), Ru(II), V(IV), and V(V),
Y is an alkali metal ion or an alkaline earth metal ion (such as K^+),
A is an anion selected from halide, hydroxide, sulphate, cyanide oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate and nitrate;
q and b are integers of 1 or more;
c may be 0 or an integer of 1 or more;
the sum of the charges on the anions Y, CN and A multiplied by q, b and c respectively (e.g. Y x q + CN x b + A x c) satisfies the valency of M''; and

the complexing agent is an ether, a ketone, an ester, an amide, an alcohol, an urea or a combination thereof, preferably wherein the complexing agent is dimethoxyethane, tert-butyl alcohol, ethylene glycol monomethyl ether, diglyme, triglyme, ethanol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, or sec-butyl alcohol.

16. The method of any preceding claim, wherein the DMC catalyst comprises the formula:

$$M'_d[M''_e(CN)_f]_g$$

Wherein M' and M'' are as defined in claim 15, and d, e, f and g are integers, and are chosen to such that the DMC catalyst has electroneutrality,
preferably, d is 3, e is 1, f is 6 and g is 2.

17. The method of claims 15 or 16 wherein M' is selected from Zn(II), Fe(II), Co(II) and Ni(II) and/or M'' is selected from Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III) and Ni(II), preferably M' is Zn(II) and M'' is Co(III).

18. The method of claims 15 to 18, wherein the DMC catalyst additionally comprises water, an organic complexing agent and/or a metal salt.

19. A polymerisation system for the copolymerisation of carbon dioxide and an epoxide, comprising:
    a. A catalyst of formula (I) as defined in any preceding claim,
    b. A DMC catalyst as defined in any preceding claim, and
    c. A starter compound as defined in any preceding claim.

20. A polycarbonate ether polyol prepared by the method of any of claims 1 to 18, wherein the polycarbonate ether polyol has n ether linkages and m carbonate linkages, wherein n and m are integers, and wherein m/(n+m) is from 0.05 to 0.95.

21. A polyurethane or other polymer prepared from a polycarbonate ether polyol as defined in claim 20.