PROCESS

TECHNICAL FIELD

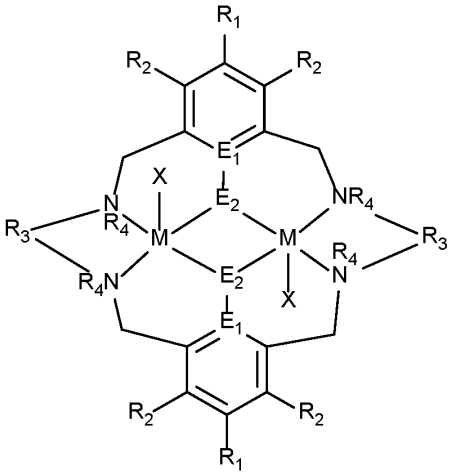
The present invention relates to a catalyst, a polymerisation process for the reaction of carbon dioxide with an epoxide in the presence of a catalyst, and to a number of uses and applications.

BACKGROUND

The ring-opening copolymerization of epoxides and carbon dioxide is a useful means of converting waste into valuable and commercially attractive polymers such as polycarbonates, polycarbonate ethers, polyether carbonates, polycarbonate ether polyols, polyether carbonate polyols, polyether polyols, polycarbonate polyols, polyester polyols, or copolymers (block or random) containing carbonate linkages. These may be high molecular weight polymers or, if a starter compound (chain transfer agent) is used, low molecular weight polymers / oligomers, such as polyols and surfactants (non-ionic, ionic and zwitterionic), amongst others. The polymer products of the ring-opening copolymerization of epoxides and carbon dioxide are useful building blocks for the production of higher polymers such as polyurethanes, or other useful products such as surfactants or lubricants. In turn these higher polymers may be use in the production of useful end-products, such as coatings, resins, foams, thermoplastic polyurethane (TPU) or thermoplastic elastomers (TPE).

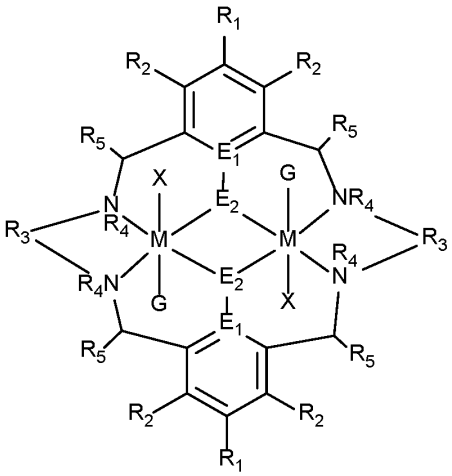
The ring-opening copolymerization reaction is frequently limited by low catalytic activities, poor tolerance to a large excess of starter compound, and a tendency to form by-products in undesirable side-reactions. Otherwise, suitable catalysts may be expensive and/or difficult to manufacture, and in some cases present processing challenges due to low solubility. The development of effective catalysts to make such a process commercially viable has been the subject of continuous research.

In WO2009/130470 the copolymerisation of an epoxide with CO_2 using a catalyst of a class represented by formula (a) was described:



Formula (a)

WO2013/034750 discloses the copolymerisation of an epoxide with CO_2 in the presence of a starter compound using a catalyst of a class represented by formula (b):

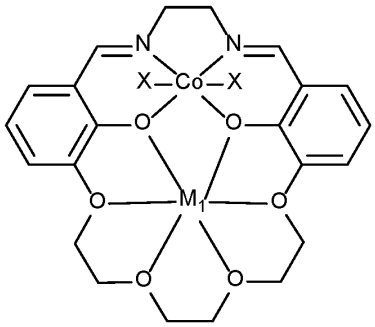


Formula (b)

These catalyst systems are fully closed, i.e. the structure around the bimetallic centre forms a 'cage' that fully surrounds the bimetallic centre. Further bimetallic heterodinuclear complexes having a fully closed 'cage' structure are described in WO2023/175340 and WO2022/008919.

Recently, Deacy *et al.*, 'Co(III)/Alkali-Metal(I) Heterodinuclear Catalysts for the Ring-Opening Copolymerization of CO_2 and Propylene Oxide', *J. Am. Chem. Soc.*, 2020, 142 (45), 19150-19160,

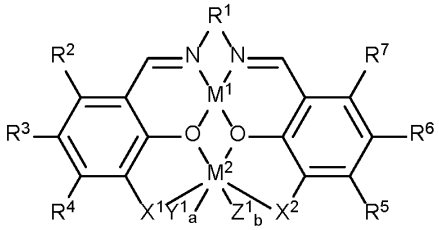
disclosed a heterodinuclear catalyst of formula (c) capable of operating at a 'low' pressure for the ring-opening copolymerisation of propylene oxide (PO) and CO_2, which may be used with a starter compound to provide molecular weight control.



Formula (c)

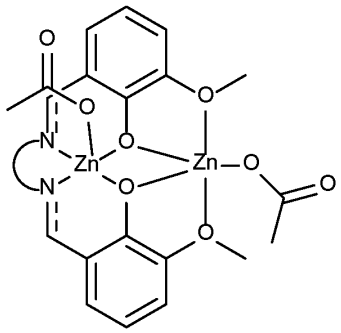
Mechanistic studies of the catalyst were conducted, and the results, detailed in Deacy et al., 'Insights into the Mechanism of Carbon Dioxide and Propylene Oxide Ring-Opening Copolymerisation Using a Co(III)/K(I) Heterodinuclear Catalyst', *J. Am. Chem. Soc.*, 2022, 144, 17929-17938, showed that the heterodinuclear catalyst is able to effect polymerisation without the presence of a co-catalyst, as each metal is individually responsible for activating or stabilising the starting materials or intermediates, lowering the energy barrier for polymerisation.

JP2013163772 discloses the copolymerisation of an epoxide with CO_2 in the presence of a catalyst of a class represented by formula (d) (M^1 is Zn, M^2 a group 6 metal):



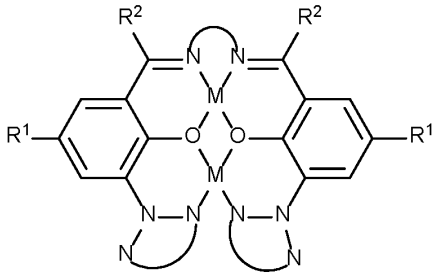
Formula (d)

Thevenon *et al.*, 'Dinuclear Zinc Salen Catalysts for the Ring Opening Copolymerization of Epoxides and Carbon Dioxide or Anhydrides', *Inorg. Chem.*, 2015, 54, 11906-11915, discloses the copolymerisation of CHO with CO_2 or anhydrides in the presence of zinc catalysts of formula (e):

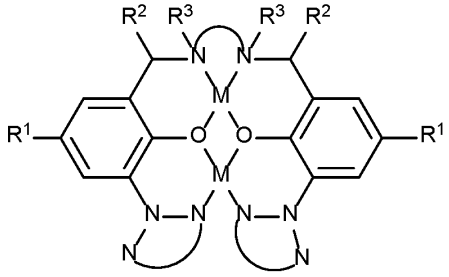


Formula (e)

Lin *et al*., 'Bimetallic Nickel Complexes that Bear Diamine-Bis(Benzotriazole Phenolate) Derivatives as Efficient Catalysts for the Copolymerization of Carbon Dioxide with Epoxides', *ChemCatChem*, 2016, *8*, 984-991, discloses the copolymerisation of CHO and its derivatives with CO_2 in the presence of catalysts according to formulas (f) and (g):



Formula (f)



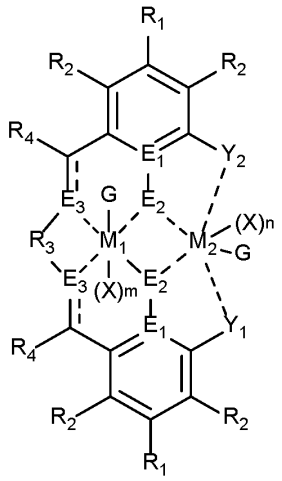
Formula (g)

Each of JP2013163772, Thevenon *et al* and Lin *et al* exemplify the copolymerisation of cyclohexene oxide with CO_2 in the presence of catalysts according to formulae (d), (e) and (f) and (g), respectively.

Each of catalysts of formulae (d), (e), (f) and (g) are open at one side of the bimetallic centre, i.e. the structure around the bimetallic centre does not form a 'cage' that fully surrounds said bimetallic centre. None of these documents disclose the use of a starter compound.

It is known that the use of starter compounds in the copolymerisation of carbon dioxide with an epoxide and/or an anhydride with an epoxide can poison the catalysts used in said copolymerisation.

WO2019048878 discloses an open-structured (i.e. non-macrocyclic) catalyst having the formula (i):



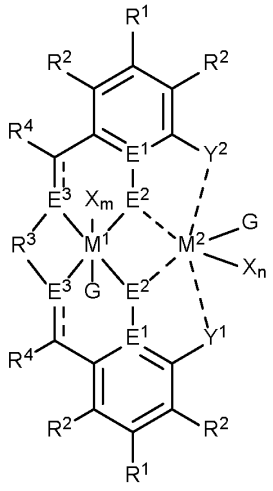
Formula (i)

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), Co(III), Mn(III), Ni(III), Fe(III), Ca(II), Ge(II), Al(III), Ti(III), V(III), Ge(IV), Y(III), Sc(III) or Ti(IV), and wherein the catalyst is used in a polymerisation process for the reaction of carbon dioxide with an epoxide, and/or an anhydride with an epoxide, in the presence of a starter compound.

The inventors have now identified a new class of heterodinuclear bimetallic catalysts having an open cage structure with at least one metal centre selected from alkali and/or alkaline earth metals (preferably alkali metals) which are relatively straightforward to synthesise with satisfactory yields, and which have generally good solubility in polymerisation reaction media, such as propylene oxide, as well as improved processability and catalytic activity with respect to the aforementioned open cage structure catalysts comprising two transition and/or main block metal centres.

SUMMARY OF THE INVENTION

According to a first aspect of the present invention, there is provided a bimetallic heterodinuclear catalyst of formula (I):



Formula (I)

wherein R^1 and R^2 are independently selected from hydrogen, halide, a nitro group, a nitrile group, an imine group, -$NCR^{13}R^{14}$, an amine, an ether –OR^{15}, –$R^{16}OR^{17}$, an ester group –$OC(O)R^{10}$ or –$C(O)OR^{10}$, an amido group –$NR^9C(O)R^9$ or –$C(O)$-$NR^9(R^9)$, -COOH, -$C(O)R^{15}$, –$OP(O)(OR^{18})(OR^{19})$,–$P(O)R^{20}R^{21}$, -$P(O)(OR)(OR)$, -$OP(O)R(OR)$, 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^4 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

R^9, R^{10}, R^{13}, R^{14}, R^{18}, R^{19}, R^{20} and R^{21} are independently selected from hydrogen or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group;

E^1 is C, E^2 is O, S or NH or E^1 is N and E^2 is O;

E^3 is N, NR^5, O or S, wherein when E^3 is N, ------ is ═══, and when E^3 is NR^5, O or S, ------ is ———;

R^5 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl, -alkylC(O)OR^{10}, -alkylnitrile, 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, nitro, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

m and n are integers between 0-3, such that the sum of m and n is between 0-4

R^x is independently selected from hydrogen or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group;

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

Y^1 and Y^2 are independently a neutral or anionic donor group capable of donating at least one lone pair to the metal M^2 selected from a group with the at least one lone pair donated by a nitrogen atom (aromatic or non-aromatic), a group with the at least one lone pair donated by a carbene carbon atom, a group with the at least one lone pair donated by an ether group oxygen atom, a group with the at least one lone pair donated by a carbonyl oxygen atom and a group with the at least one lone pair donated by a carboxylate oxygen atom; and

at least one of M^1 and M^2 is an alkali or alkaline earth metal.

It will be appreciated from the structure of Formula (I) that the ligand surrounding the metal centres has an open 'cage' structure rather than a closed 'cage' structure. The open structure results from the Y^1 and Y^2 groups not being linked to each other to form a single group, but rather being distinct groups within the structure.

M^1 and M^2 are preferably independently selected from transition and/or main block metals and/or alkali or alkaline earth metals, wherein when M^1 is a transition and/or main block metal, M^2 is an alkali or alkaline earth metal, or wherein when M^1 is an alkali or an alkaline earth metal, M^2 is a transition and/or main block metal.

Preferably when one of M^1 and M^2 is Mg, the other of M^1 and M^2 is not a transition metal or main block metal.

Preferably M^1 is a transition metal or main block metal, whilst M^2 is an alkali or alkaline earth metal.

According to a second aspect of the present invention, there is provided the use of a bimetallic heterodinuclear catalyst of formula (I) above in the manufacture of polymers, particularly polymers

containing carbonate linkages, for example copolymers (block or random) containing carbonate linkages. Such polymers may for example include polycarbonates, polycarbonate ethers, polyether carbonates, polycarbonate ether polyols, polyether carbonate polyols, polyether polyols, polycarbonate polyols and polyester polyols.

Such polymers may have the formula (II):

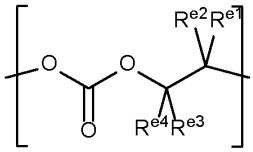
$$Z^1\text{-}((PC)_P\text{-}(PE)_Q\text{-}Z^2)_X \qquad (II)$$

wherein:

Z^1 is either derived from a starter compound or from X (as defined in formula (I));

the or each Z^2 is independently an ionic species, or OH, O-R', O-C(O)-R' or O-C(O)-O-R', wherein R' is an optionally substituted hydrocarbyl or heterohydrocarbyl;

PC represents a carbonate block with P repeat units of formula:

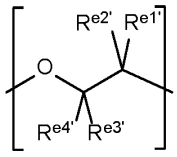


;

wherein:

R^{e1}, R^{e2}, R^{e3}, and R^{e4} are each independently selected from H, halogen, hydroxyl, or optionally substituted hydrocarbyl or heterohydrocarbyl;

PE represents a polyether block with Q repeat units of formula:



;

wherein:

$R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ are each independently selected from H, halogen, hydroxyl, or optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, heteroalkyl or heteroalkenyl;

wherein the value of the or each P is independently 1 or above;

wherein the value of the or each Q is independently 0 or above; and

X is 1 or more.

When Z is derived from a starter compound it preferably has the formula R, R-O, R-C(O)-O or R-O-C(O)-O, wherein R is an optionally substituted hydrocarbyl or heterohydrocarbyl group, or R-NR', R–S, wherein R' is H, or optionally substituted hydrocarbyl or heterohydrocarbyl group), or wherein Z is a phosphate, phosphinate, phosphonate, phosphite or hypophosphite derivative.

When Z is derived from X (an initiating group on the catalyst of formula (I)) then Z is preferably selected from R^x-C(O)-O, R^x-$S(O)_2$-O, R^x-S(O)-O, $(R^x)_2$-S(O)-O, R^x(O)S, R^x-O, phosphinate, halide, nitrate, hydroxyl, carbonate, amino, nitro, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl, wherein R^x is as defined in formula (I).

R and R' may each independently be straight or branched chain, cyclic or acyclic, aromatic, or non-aromatic. Alkyl groups are preferred, in particular C_1-C_{11} alkyl groups.

Preferably R^{e1} is selected from H or optionally substituted alkyl; and R^{e2}, R^{e3} and R^{e4} are each independently selected from H, halogen, hydroxyl, or optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, heteroalkyl or heteroalkenyl.

Preferably one of R^{e1}, R^{e2}, R^{e3}, and R^{e4} is methyl, ethyl, propyl, butyl, or an ether, ester, or carbonate group, and the remaining three of R^{e1}, R^{e2}, R^{e3}, and R^{e4} are all H.

R^{e1} and R^{e2} and/or R^{e3} and R^{e4} may together form a saturated, partially unsaturated, or unsaturated ring containing carbon and hydrogen atoms, and optionally one or more heteroatoms (e.g. O, N or S). For example, R^{e1} and R^{e2} and/or R^{e3} and R^{e4} may together form a 5 or six membered ring.

Preferably $R^{e1'}$ is selected from H or optionally substituted alkyl; and $R^{e2'}$, $R^{e3'}$ and $R^{e4'}$ are each independently selected from H, halogen, hydroxyl, or optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, heteroalkyl or heteroalkenyl.

Preferably one of $R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ is methyl, ethyl, propyl, butyl, or an ether, ester or carbonate group, and the remaining three of $R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ are all H.

$R^{e1'}$ and $R^{e2'}$ and/or $R^{e3'}$ and $R^{e4'}$ may together form a saturated, partially unsaturated, or unsaturated ring containing carbon and hydrogen atoms, and optionally one or more heteroatoms (e.g. O, N or S). For example, $R^{e1'}$ and $R^{e2'}$ and/or $R^{e3'}$ and $R^{e4'}$ may together form a 5 or six membered ring.

The polymer may be a high molecular weight polymer – in which case the or each P and/or the or each Q may be for example be up to about 1,000 or up to about 500, for example.

Alternatively, the polymer may be a low molecular weight polymer or oligomer – in which case the or each P and/or the or each Q may be less than about 50, for example.

In this specification "hydrocarbyl or heterohydrocarbyl" includes alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, heterocycloalkyl, heterocycloalkenyl, aryl, heteroaryl, heteroalkyl, heteroalkenyl or heteroalkynyl, and any combination of any of these groups, for example alkylaryl, heteroalkylaryl, heteroalkylheteroaryl or alkylheteroaryl.

In one of its aspects the invention provides the use of a bimetallic heterodinuclear catalyst of formula (I) to manufacture a copolymer comprising carbonate linkages and at least one other type of linkage. Preferably carbonate linkages provide ≤85 wt.% of the total linkages. One or more co-catalysts may be used, for example an ether co-catalyst (DMC for example), to facilitate the formation of non-carbonate linkages such as ether linkages.

In the polymers of formula (II), the adjacent monomer units in the backbone may be head-to-tail linkages, head-to-head linkages, or tail-to-tail linkages.

It will also be appreciated that formula (II) does not require the carbonate links and the ether links (when present) to be present in two distinct "blocks", but instead the carbonate and ether (when present) repeating units may be statistically distributed along the polymer backbone, or may be arranged so that the carbonate and ether linkages (when present) are not in two distinct blocks.

Thus, the polymer of formula (II)) may be referred to as a random copolymer, a statistical copolymer, an alternating copolymer, or a periodic copolymer. It may of course alternatively be a block copolymer.

Further detail concerning these polymers and their methods of manufacture with other catalysts is taught in our WO2017037441A1, and also the methods described in WO2019081931A1, or in US2018044464A1, for example. Other methods will be apparent to the skilled addressee, based on the reaction of an alkylene oxide with CO_2 in the presence of suitable starter(s) and catalyst(s).

Such polymers preferably have greater than 10 wt.% CO_2 incorporation, more typically, greater than 15, 20 or 21 wt.% CO_2 incorporation, preferably 10 to 40 wt.% CO_2 incorporation, typically, 15 to 40 wt.% CO_2 incorporation, more typically, 20 to 40 wt.% CO_2 incorporation. The preferred degree of wt.% CO_2 incorporation depends on the end application – typically 10-25 wt.% is a preferred range for polyols – 20-35 wt.% for surfactants.

According to a third aspect of the present invention there is provided the use of a bimetallic heterodinuclear catalyst of formula (I) above in the manufacture of polymers.

According to a fourth aspect of the present invention there is provided the use of a bimetallic heterodinuclear catalyst of formula (I) above in the manufacture of polyols.

According to a fifth aspect of the present invention there is provided the use of a bimetallic heterodinuclear catalyst of formula (I) above in the manufacture of surfactants.

There is also provided a process for producing such polymers comprising reacting carbon dioxide, or a source of carbon dioxide, and an epoxide in the presence of a catalyst of formula (I).

The process of the invention may comprise reacting the carbon dioxide and the epoxide also in the presence of a starter compound.

The starter compound when used facilitates the synthesis of polymers with defined molecular weights, structures, and end groups for further reactivity.

The process of the invention may comprise reacting carbon dioxide and the epoxide also in the presence of a solvent. Examples of suitable solvents include, but are not limited to, ethyl acetate, propyl acetate, butyl acetate, acetone, toluene, diethyl carbonate, dimethyl carbonate, dioxane, dichlorobenzene, methylene chloride, propylene carbonate and ethylene carbonate.

The process of the invention may comprise contacting carbon dioxide and the epoxide – and/or the reaction product of the reaction between carbon dioxide and the epoxide - with a co-catalyst.

The co-catalyst may for example be an ether catalyst.

Suitable ether catalysts, including DMC, are widely known in the art, and discussed for example in our WO2023072843, the contents of which are hereby incorporated by reference.

When a co-catalyst is used in the process of the invention, the process may be conducted in a single reaction zone wherein the reaction mixture is exposed to both the catalyst of formula (I) and the co-catalyst in the reaction zone; or in multiple reaction zones wherein the reaction mixture is exposed to the catalyst of formula (I) in a proximal reaction zone and to the co-catalyst in a distal reaction zone. Nothing aforesaid prevents use of the catalyst of formula (I) as well in the distal reaction zone and/or the use of a co-catalyst as well in the proximal reaction zone.

According to a sixth aspect of the present invention there is provided a polymer produced by the aforesaid process. The polymer may for example be a polyol (useful as a polyurethane precursor) or a surfactant.

The present invention also relates to the use of a polyol molecule obtainable by the methods discussed above as a precursor in the manufacture of higher polymers – polyurethanes, for example.

The present invention also relates to the use of a surfactant molecule obtainable by the methods discussed above in a cleaning product and a composition comprising said surfactant molecule where the composition is a surfactant formulation for a cleaning product.

The surfactant molecule prepared by the methods of the invention may also be used as a functional additive in personal care products, agrichemicals, enhanced oil recovery, construction materials in the nature of foams, coatings, paints, adhesives, automotive applications, and textile manufacture. Suitable compositions for use in such applications may be formulated comprising the surfactant molecule of the invention.

According to a seventh aspect of the present invention there is provided a higher polymer produced using the polymer of the fifth aspect of the present invention.

In preferred embodiments of the seventh aspect, the higher polymer may be a polyurethane, a polyurea or a polyamine.

In a preferred embodiment of the first aspect of the present invention, when M^1 or M^2 is a transition and/or main block metal, the transition and/or main block metal centres may be selected from Zn(II), Cr(II), Co(II), Cu(II), Mn(II), Mg(II), Ni(II), Fe(II), Ti(II), V(II), Cr(III), Co(III), Mn(III), Ni(III), Fe(III), Ge(II), Al(III), Ti(III), V(III), Ge(IV), Y(III), Sc(III) or Ti(IV).

In a preferred embodiment of the first aspect of the present invention, when M^1 or M^2 is an alkali or alkaline earth metal, the alkali or alkaline earth metal centres may be selected from Li(I), Na(I), K(I), Rb(I), Cs(I), Fr(I), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Ra(II).

Mixed metal catalysts of the form transition and/or main block metal-alkali/alkaline earth metal, exploit the high nucleophilicity of transition and/or main block metal carbonate intermediates and the oxophilicity of the alkali/alkaline earth metals toward epoxide coordination. Additionally, alkali/alkaline earth metals are attractive due to their abundance, low cost, lack of colour, and low toxicity.

In a most preferred embodiment when M^1 or M^2 is an alkali or alkaline earth metal, the alkali or alkaline earth metal centre is K(I) or Na(I).

In a preferred embodiment of the invention, Y^1 and Y^2 may each independently be selected from a group wherein the or each lone pair is donated by an ether group oxygen atom. Y^1 and Y^2 may each for example be an ether chain comprising more than one oxygen atom, each oxygen atom donating a lone pair to the metal centre.

In certain preferred embodiments of the invention the epoxide comprises at least one epoxide other than propylene oxide. Preferably the at least one epoxide comprises ethylene oxide in that case. More preferably, the at least one epoxide comprises substantially only ethylene oxide. (By “substantially” we mean that epoxides other than ethylene oxide are present in the at least one epoxide in an amount of less than about 10 wt.%, preferably less than about 5 wt.%, for example less than about 2 wt. %, typically about zero or zero wt.% of all epoxides present in the reaction mixture.)

DETAILED DESCRIPTION

Catalyst

In the catalyst of formula (I) each occurrence of R^1 can be the same or different, and R^1 and R^2 can be the same or different. Preferably, each occurrence of R^1 is the same. Preferably, each occurrence of R^2 is the same. When R^1 and R^2 are the same, preferably each occurrence of R^1 and R^2 is methyl. Preferably, each occurrence of R^1 is the same, and each occurrence of R^2 is the same, and R^1 is different from R^2.

Preferably, R^1 and R^2 may be independently selected from hydrogen, halide, amino, nitro, sulfoxide, sulfonyl, sulfinate, silyl, silyl ether and an optionally substituted alkyl, alkenyl, aryl, heteroaryl, heteroalicyclic, alkoxy, aryloxy or alkylthio. Preferably, each occurrence of R^2 is the same, and is hydrogen.

Even more preferably, R^2 is hydrogen and R^1 may be independently selected from hydrogen, halide, amino, nitro, sulfoxide, sulfonyl, sulfinate, silyl, silyl ether and optionally substituted alkyl, alkenyl, aryl, heteroaryl, heteroalicyclic, alkoxy, aryloxy, alkylthio, arylthio, such as hydrogen, $C_{1\text{-}6}$alkyl (e.g. haloalkyl), alkoxy, aryl, halide, nitro, sulfonyl, silyl and alkylthio, for example t-butyl, n-butyl, i-propyl, methyl, piperidinyl, methoxy, hexyl methyl ether, $-SCH_3$, $-S(C_6H_5)$, nitro, trimethylsilyl, methylsulfonyl ($-SO_2CH_3$), triethylsilyl, halogen or phenyl.

Preferably, both occurrences of R^1 are the same, and may be selected from hydrogen, halide, amino, nitro, sulfoxide, sulfonyl, sulfinate, silyl, silyl ether and an optionally substituted alkyl, alkenyl, aryl, heteroaryl, heteroalicyclic, alkoxy, aryloxy, or alkylthio. More preferably, both occurrences of R^1 are the same, and may be selected from halide, sulfoxide, silyl, and an optionally substituted alkyl, heteroaryl or alkoxy. Still more preferably, both occurrences of R^1 are the same, and may be selected from H, alkyl, aryl, alkoxy, trialkylsilyl such as triethylsilyl, or halide. More preferably still, both occurrences of R^1 are the same, and may be selected from H, alkyl, phenyl, halide or trialkylsilyl. Most preferably, both occurrences of R^1 are the same, and may be selected from H, methyl, ethyl, n-propyl, i-propyl n-butyl, t-butyl, t-amyl or t-octyl.

It will be appreciated that the group R^3 can be the divalent alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene or heteroalkynylene group which may optionally be interrupted by an aryl, heteroaryl, alicyclic or heteroalicyclic group, or may be a divalent arylene or cycloalkylene group which acts as a bridging group between two nitrogen centres. Thus, where R^3 is an alkylene group, such as 2,2-dimethylpropane-1,3-diyl, the R^3 group has the structure $–CH_2\text{-}C(CH_3)_2\text{-}CH_2\text{-}$. The definitions of the alkyl, aryl, cycloalkyl etc groups set out herein therefore also relate respectively to

the divalent alkylene, arylene, cycloalkylene etc groups set out for R^3, and may also be optionally substituted. Exemplary options for R^3 include ethane-1,2-diyl, 2,2-fluoropropane-1,3-diyl, 2,2-dimethylpropane-1,3-diyl, propane-1,3-diyl, butane-1,4-diyl, phenylene, cyclohexane-1,2-diyl, cyclohexane-1,4-diyl or biphenylene. When R^3 is cyclohexane-1,2-diyl or cyclohexane-1,4-diyl, it can be the racemic, RR- or SS- forms.

R^3 may be independently selected from substituted or unsubstituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene or heteroalkynylene, arylene or cycloalkylene. Preferably, R^3 may be selected from substituted or unsubstituted alkylene, cycloalkylene, alkenylene, heteroalkylene and arylene. More preferably, R^3 may be selected from $–CH_2C(CH_3)_2CH_2$-, $-CH_2CH_2CH_2$-, $-CH_2CH(CH_3)CH_2$-, $-CH_2C(CH_2C_6H_5)_2CH_2$-, $–(C_6H_4)$-, $-CH_2CH_2$-, $-CH_2-CH_2CH_2CH_2$-, $-CH_2CH_2N(CH_3)CH_2CH_2$-, $–(C_6H_{10})$- or $-CH_2CH_2CH(C_2H_5)$-. Still more preferably R^3 may be selected from $–CH_2C(CH_3)_2CH_2$-, $-CH_2CH_2$-, $-CH_2CH_2CH_2$-, $-CH_2CH(CH_3)CH_2$-, $-CH_2C(CH_2C_6H_5)_2CH_2$-, $-CH_2CH_2CH(C_2H_5)$-, $-CH_2CH_2CH_2CH_2$-. More preferably still, R^3 may be selected from $–CH_2C(CH_3)_2CH_2$-, $-CH_2CH_2CH_2$-, $-CH_2CH(CH_3)CH_2$- and $-CH_2C(C_2H_5)_2CH_2$-.

Preferably, each R^4 may be independently selected from hydrogen, and optionally substituted aliphatic or aryl. More preferably, each R^4 may be independently selected from hydrogen or optionally substituted alkyl or aryl. Even more preferably, each R^4 is the same, and may be selected from hydrogen or optionally substituted alkyl or aryl. Exemplary R^4 groups may include hydrogen, methyl, ethyl, n-propyl, n-butyl, phenyl and trifluoromethyl, preferably hydrogen, methyl or trifluoromethyl. Even more preferably, each R^4 is hydrogen.

In preferred combinations of the R^4 group and R^1 group, R^1 may be selected from H, methyl, ethyl, n-propyl, n-butyl, t-butyl, t-octyl, Cl, Br, F, nitro, trimethylsilyl, triethylsilyl, methylthio and methoxy and R^4 may be selected from H, methyl, ethyl, n-propyl, phenyl and trifluoromethyl.

Each occurrence of E^1 may be the same or different. Preferably, each occurrence of E^1 is the same. Each occurrence of E^2 may be the same or different. Preferably, each occurrence of E^2 is the same. Preferably, E^1 is C and E^2 is O, S or NH more preferably E^1 is C and E^2 is O.

Each occurrence of E^3 may be the same or different. Preferably, each occurrence of E^3 is the same. Preferably R^5, when present, may be independently selected from hydrogen or optionally substituted alkyl, alkenyl, alkynyl, aryl, heteroaryl, heteroalkenyl, heteroalkynyl, heteroaryl, -alkyl$C(O)R^{10}$ or -

alkylnitrile. Each R^5, when present, may be the same or different. Preferably, R^5, when present, may be selected from hydrogen or optionally substituted alkyl, alkenyl, alkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl or heteroaryl. More preferably, each R^5, when present, is the same and may be selected from hydrogen or optionally substituted alkyl, alkenyl, alkynyl, aryl, heteroalkyl, heteroalkenyl, heteroalkynyl or heteroaryl. Exemplary R^5 groups include H, Me, Et, Bn, iPr, tBu or Ph. Even more preferably, each R^5, when present, is hydrogen or alkyl. Most preferably, each R^5, when present, is hydrogen. Preferably, E^3 is N.

Y^1 and Y^2 are groups which are capable of donating at least one lone pair of electrons to the metal M^2. The atom(s) of the Y^1 group which donate the one or more lone pairs of elections typically form a bond between Y^1 and the metal, M^2. Likewise, the lone pair-donating atoms(s) of the Y^2 group.

Y^1 and Y^2 may be the same or different. Preferably, Y^1 and Y^2 are the same. The atom(s) of the Y^1 and/or Y^2 group that donates the lone pair(s) is typically a hetero atom selected from oxygen, nitrogen, or sulphur or a carbene carbon.

Accordingly, Y^1 and Y^2 may be hetero or a group containing a heteroatom capable of donating one or more lone pairs. Typically, the or each lone pair is provided by a nitrogen, sulphur, or oxygen atom, more typically by a nitrogen or oxygen atom, most typically by an oxygen atom.

Y^1 and Y^2 may independently comprise from 1 to 20 atoms, preferably from 1 to 15 atoms, more preferably from 1 to 12 atoms.

Preferably, Y^1 and Y^2 may be independently selected from O^-, S^-, $^-N(R^{10})C(O)R^{10}$, $-C(O)O^-$, $-C(O)OR^{10}$, $-C(O)R^{10}$, $-C(R^{10})_2C(O)N(R^{10})_2$, $-OR^{10}OR^{10}$, optionally substituted heteroaliphatic such as $-OR^{10}$, $-SR^{10}$, $-^-NR^{10}$, $-N(R^{10})_2$, $-C(R^{10})_2N(R^{10})_2$, $-C(R^{10})N(R^{10})$, or optionally substituted heteroalicyclic or heteroaryl or an optionally substituted carbene structure, wherein each R^{10} may be independently selected from hydrogen or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group. More preferably, Y^1 and Y^2 may be independently selected from O^-, S^-, $-OR^{10}$, $-SR^{10}$, $-^-N(R^{10})$, $-N(R^{10})_2$, $-OR^{10}OR^{10}$, $-C(R^{10})_2N(R^{10})_2$, $-C(R^{10})N(R^{10})$, $^-N(R^{10})C(O)R^{10}$, $-C(O)O$, $-C(O)OR^{10}$, $C(O)R^{10}$ or optionally, imidazoline, 'abnormal' imidazoline (wherein the 'abnormal' imidazoline has a positive and a negative charge on the heterocycle due to the position of the double bond), imidazolidine, pyrrolidine, pyrroline, triazoline, thiazoline oxazole, oxazoline, imidazoylidene, imidazolinylidene, thiazolylidene, oxazolylidene, triazolylidene, benzimidazolylidene, pyrrolidinylidene or 'abnormal imidazolylidene or

N,N'-diamidocarbene, optionally substituted pyridine, imidazole, methyl imidazole, benzimidazole, pyrrole, triazole, thiazole, benzimidazoline, benzotriazole, wherein R^{10} may be independently selected from hydrogen or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group.

When Y^1 and Y^2 are selected from optionally substituted heteroaliphatic, heteroalicyclic or heteroaryl, they contain one or more hetero atom(s) capable of donating a lone pair to metal M^2. When Y^1 and Y^2 are independently selected from an optionally substituted carbene structure which may or may not be heteroaliphatic, heteroalicyclic or heteroaryl, the optionally substituted carbene structure may contain a carbon atom that is capable of donating the lone pair to metal M^2.

Still more preferably, Y^1 and Y^2 may be independently selected from O^-, $-OR^{10}$, $-N(R^{10})_2$, $-OR^{10}OR^{10}$, $-C(R^{10})_2N(R^{10})_2$, $-C(R^{10})N(R^{10})$, $-C(O)O^-$, $-C(O)R^{10}$, optionally substituted imidazolylidene, benzimidazolylidene, imidazolinylidene, or pyrrole.

Most preferably, Y^1 and Y^2 may be independently selected from O, $-OCH_3$ -C(=O)H, from ethers or amines – for example $-OCH_2CH_2OMe$, $-OCH_2CH_2OPh$, $-OCH_2CH_2OiPr$, $-OCH_2CH_2OEt$, $-OCH_2CH_2OnBu$ $-CH_2N(CH_3)_2$, $-CH_2N(H)(CH_2CH(CH_3)_2)$, $-CH_=N(CH_2CH(CH_3)_2)$, $-CH_2$-piperidine or benzotriazine.

The lone pair donating atom of the Y^1 and Y^2 groups may independently be attached directly to the remainder of the catalyst of formula (I), via a bond to the respective aryl group, or may be attached to the remainder of the catalyst of formula (I) via a linking group attached to the respective aryl group. Preferably, the linking group, when present in Y^1 and/or Y^2, may be selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene. More preferably, the linking group, when present in Y^1 and/or Y^2, may be selected from optionally substituted alkylene, alkenylene, alkynylene or arylene, even more preferably optionally substituted alkylene of arylene. Preferably, the linking group, when present in Y^1 and/or Y^2, may be optionally substituted C_1-C_{10} alkylene, more preferably optionally substituted C_1-C_6 alkylene, even more preferably optionally substituted C_1-C_4 alkylene, most preferably methylene. For the avoidance of doubt, when the lone pair donating atom of the in Y^1 and/or Y^2 groups is a carbene carbon, the carbene carbon may not be attached directly to the remainder of the catalyst of formula (I).

The heteroatom of the Y^1 and Y^2 groups may be attached to the respective aryl group of the remainder of the catalyst of formula (I) via the linking group (when present), by any suitable number of atoms,

preferably 1 to 10 atoms, more preferably 1 to 6 atoms, even more preferably 1 to 4 atoms, most preferably 1 to 2 atoms. It will be appreciated that when the heteroatom of the Y^1 and/or Y^2 groups is attached directly to the respective aryl group of the remainder of the catalyst of formula (I), no linking group is present.

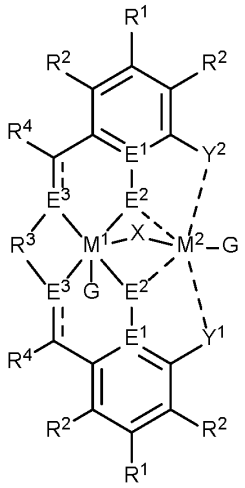
It will be appreciated that X acts as the initiating species for the processes of the present invention. Each X may be independently selected from $OC(O)R^x$, OSO_2R^x, $OSO(R^x)_2$, OR^x, halide, nitrate, hydroxyl, carbonate, amido or optionally substituted aliphatic, heteroaliphatic (for example silyl), alicyclic, heteroalicyclic, aryl or heteroaryl. R_x may be independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl. Preferably, X may be $OC(O)R^x$ or OR^x. Preferably, R^x may be independently hydrogen, optionally substituted aliphatic, haloaliphatic, aryl, heteroaryl, silyl, or alkylaryl. Exemplary options for X may include $OCOCH_3$, $OCOCF_3$, $OSO_2C_7H_7$, $OSO(CH_3)_2$, Et, Me, PhOEt, OMe, OiPr, OtBu, Cl, Br, I, F, $N(iPr)_2$ or $N(SiMe_3)_2$.

When G is not absent, it is a group which is capable of donating a lone pair of electrons (i.e. a Lewis base). Each G may be neutral or negatively charged. If G is negatively charged, then one or more positive counterions will be required to balance out the change of the complex. Suitable positive counterions may include group 1 metal ions (Na^+, K^+, etc), group 2 metal ions (Mg^{2+}, Ca^{2+}, etc), ammonium ions (i.e. $N(R^{26})_4^+$), iminium ions (i.e. $(R^{12})_2C=N(R^{26})_2^+$, such as bis(triphenylphosphine)iminium ions) or phosphonium ions ($P(R^{26})_4^+$), wherein each R^{26} may be independently selected from hydrogen or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl. Preferably, G may be independently selected from an optionally substituted heteroaliphatic group, an optionally substituted heteroalicyclic group, an optionally substituted heteroaryl group, a halide, hydroxide, hydride, a carboxylate, and water. More preferably, G may be independently selected from water, an alcohol, a substituted or unsubstituted heteroaryl (imidazole, methyl imidazole, pyridine, 4-dimethylaminopyridine, pyrrole, pyrazole, etc), an ether dimethyl ether, diethyl ether, cyclic ethers, etc), a thioether, carbene, a phosphine, a phosphine oxide, a substituted or unsubstituted heteroalicyclic (morpholine, piperidine, tetrahydrofuran, tetrahydrothiophene, etc), an amine, an alkyl amine trimethylamine, triethylamine, etc), acetonitrile, an ester (ethyl acetate, etc), an acetamide (dimethylacetamide, etc), a sulfoxide (dimethyl sulfoxide, etc), a carboxylate, a hydroxide, hydride, a halide, a nitrate, a sulfonate, etc. In some embodiments, one or both instances of G may be independently selected from optionally substituted heteroaryl, optionally substituted heteroaliphatic, optionally substituted heteroalicyclic, halide, hydroxide,

hydride, an ether, a thioether, carbene, a phosphine, a phosphine oxide, an amine, an alkyl amine, acetonitrile, an ester, an acetamide, a sulfoxide, a carboxylate, a nitrate or a sulfonate. In some embodiments, one or both instances of G may be negatively charged (for example, halide). In further embodiments, one or both instances of G may be an optionally substituted heteroaryl.

When used for the production of polycarbonate polyols, preferably formula (I) has the proviso that formula (I) is different in at least one respect to the case in which R^1, R^2 and R^4 are each hydrogen, R^3 is ethylene, E^1 is C, E^2 is O, E^3 is N, X is $OC(O)R^x$ wherein R^x is methyl, G is absent, Y^1 and Y^2 are each methoxyethoxy groups, M^1 is Co, and M^2 is K.

It will be appreciated that although in formula (I), the groups X and G are illustrated as being associated with a single M_1 or M_2 metal centre, one or more X and G groups may (instead or as well) form a bridge between the M_1 and M_2 metal centres. For example, an X group may be associated with a single M metal centre as shown in formula (I), or an X group may (particularly if neither M_1 nor M_2 are M(III)) be associated with both metal centres and form a bridge between the two metal centres, as shown below in formula (Ia):



Formula (Ia)

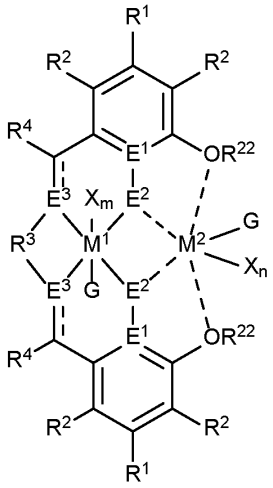
M^1 and M^2 are independently selected from transition and/or main block metals and/or alkali or alkaline earth metals, wherein when M^1 is a transition and/or main block metal, M^2 is an alkali or alkaline earth metal, and wherein M^1 is an alkali or an alkaline earth metal, M^2 is a transition and/or main block metal.

Preferably, when M^1 or M^2 is a transition and/or main block metal, the transition and/or main block metal centres may be selected from Zn(II), Cr(II), Co(II), Cu(II), Mn(II), Mg(II), Ni(II), Fe(II), Ti(II), V(II), Cr(III), Co(III), Mn(III), Ni(III), Fe(III), Ge(II), Al(III), Ti(III), V(III), Ge(IV), Y(III), Sc(III) or Ti(IV). Preferably, when a transition and/or main block metal, M^1 or M^2 may be selected from Co(III), Cr(III), Fe(III), Al(III), Zn(II), Ni(II).

Preferably, when M^1 or M^2 is an alkali or alkaline earth metal, the alkali or alkaline earth metal centres may be selected from Li(I), Na(I), K(I), Rb(I), Cs(I), Fr(I), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Ra(II).

Preferably, the catalyst has a neutral overall charge. It will be appreciated that M^1 and/or M^2 may each have one or more optional X groups co-ordinated to the metal centre depending on the oxidization state of the M^1 and M^2 metals and on the charge of the Y^1 and Y^2 groups used, wherein X is as defined above.

In some preferred embodiments, catalysts of formula (I) may have the following structure:

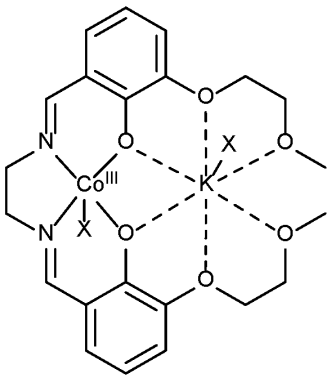


wherein each R^{22} may be independently selected from $-R^{10}$ or $-R^{10}OR^{10}$, wherein each R^{10} may be independently selected from hydrogen or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group.

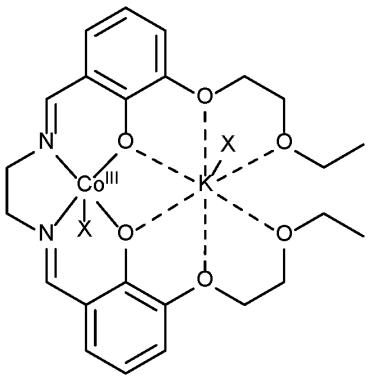
Preferably, each R^{22} is independently selected from $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$, $-CH_2CH_2OMe$, $-CH_2CH(CH_3)_2$, $-CH_2CH_2OPh$, $-CH_2CH_2OiPr$, $-CH_2CH_2OEt$, and/or $-CH_2CH_2OnBu$.

The remaining substituent groups are as defined above.

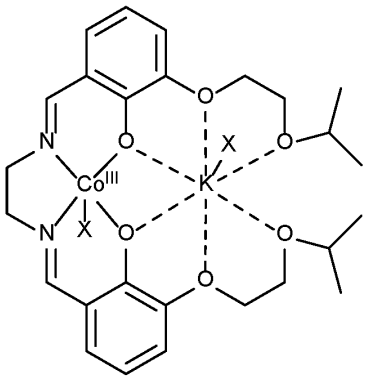
Preferable catalysts of formula (I) include, but are not limited to:



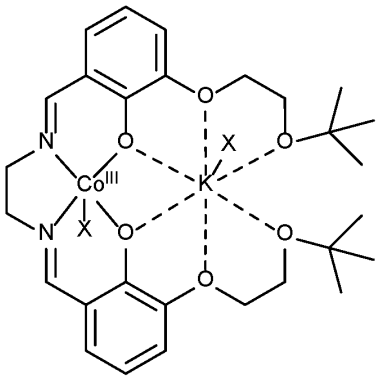
X=OAc



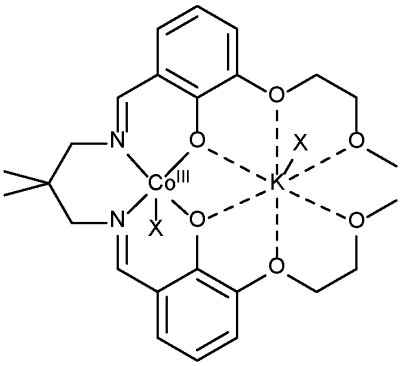
X=OAc or OMe



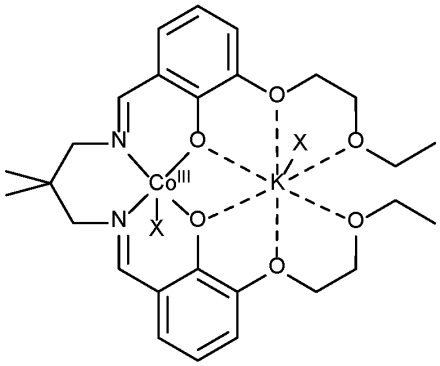
X=OAc, OMe or OEt



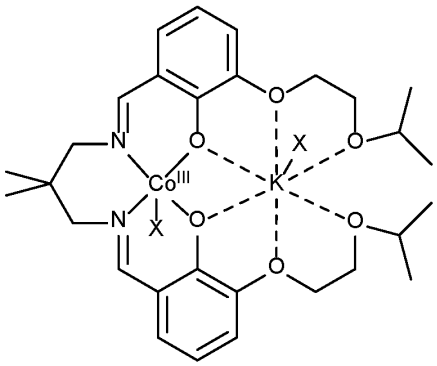
X=OAc or Cl



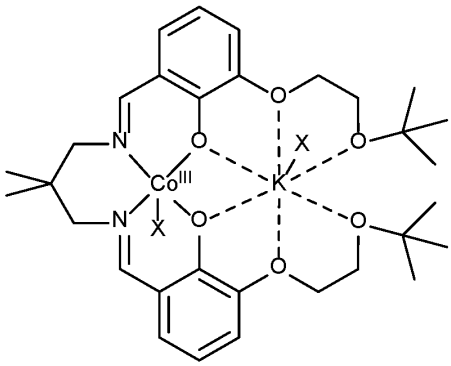
X=OAc



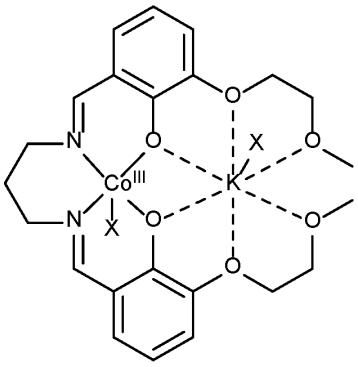
X=OAc, OPr or Cl



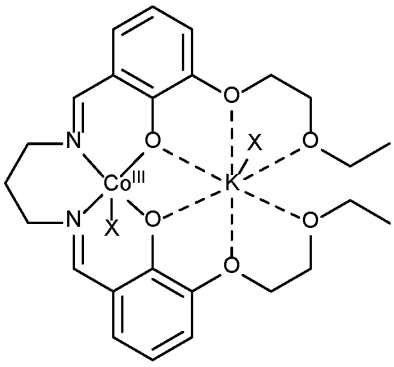
X=OAc



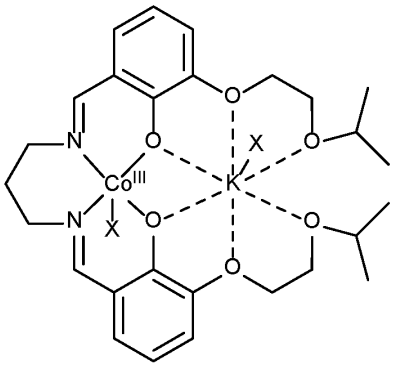
X=OAc



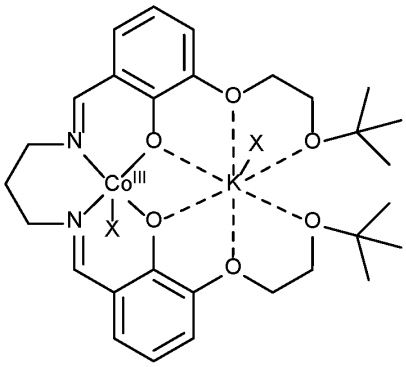
X=OAc or OBu



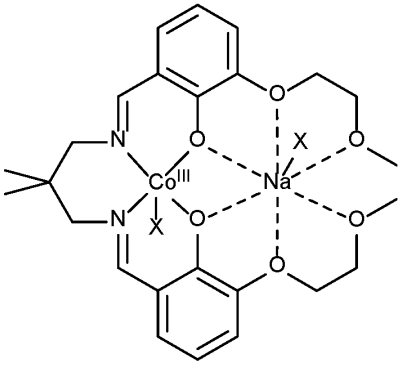
X=OAc



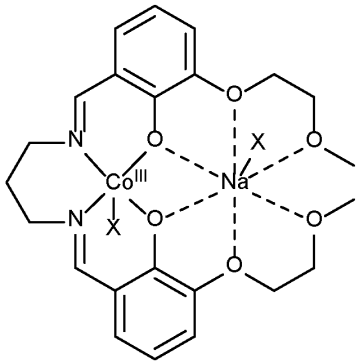
X=OAc or Cl



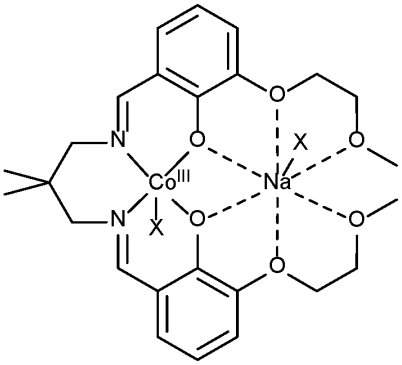
X=OAc



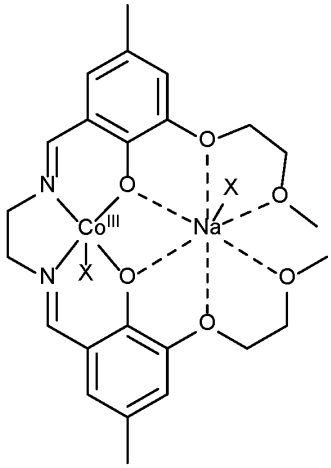
X=OAc



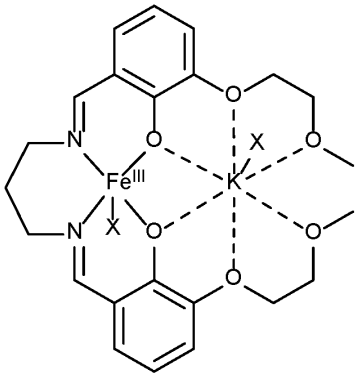
X=OAc, OMe, OPr or Cl



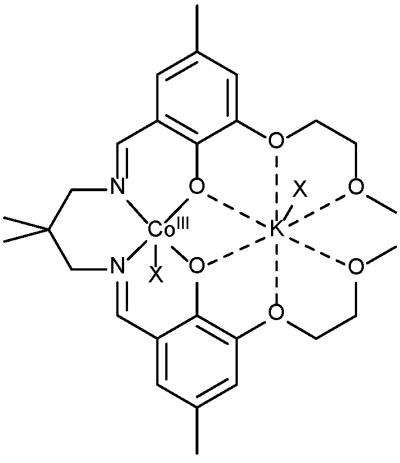
X=OAc



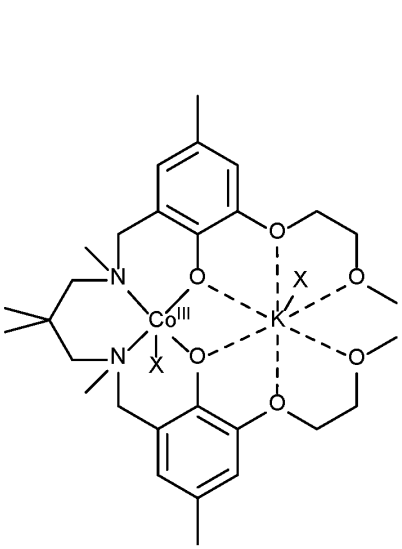
X=OAc or Cl



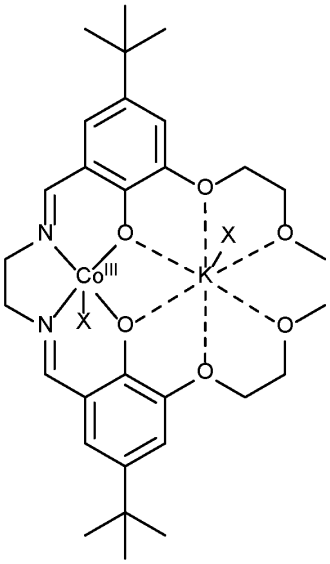
X=OAc, OCOOEt, or OMe



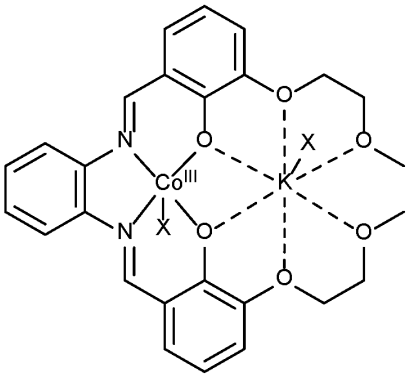
X=OAc



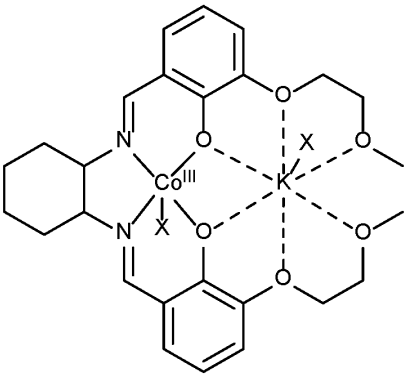
X=OAc



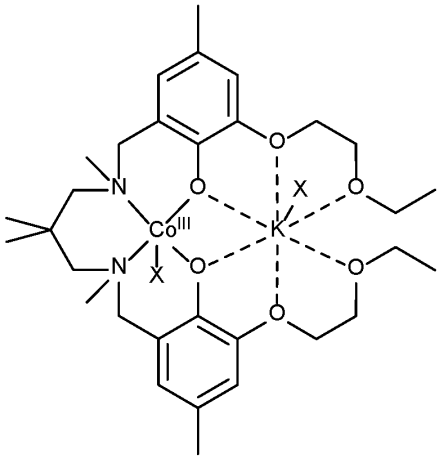
X=OAc or Cl



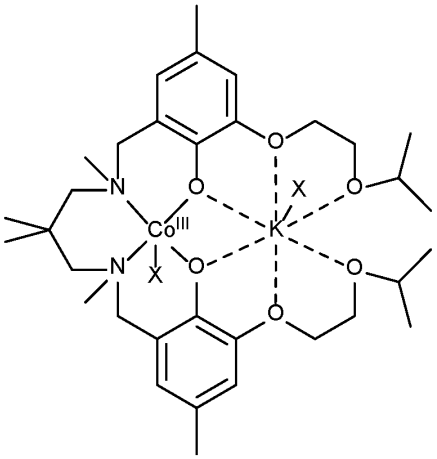
X=OAc



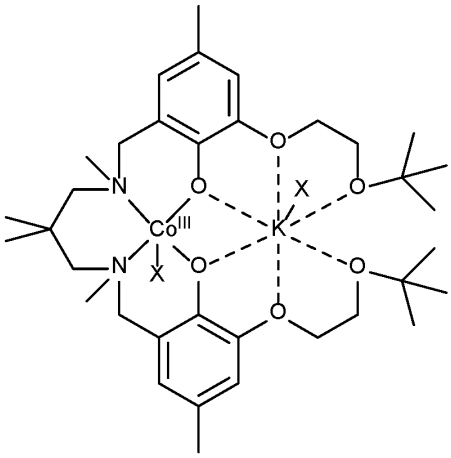
X=OAc



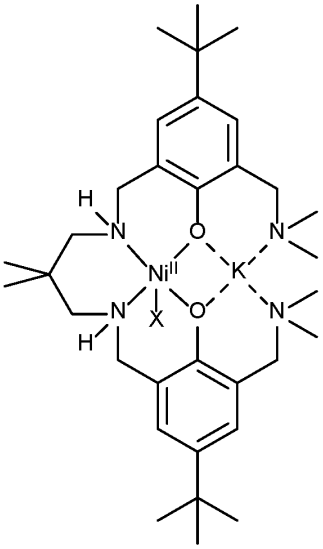
X=OAc or Cl



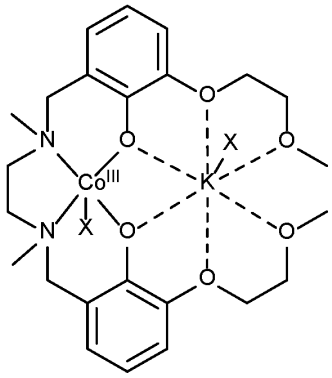
X=OAc



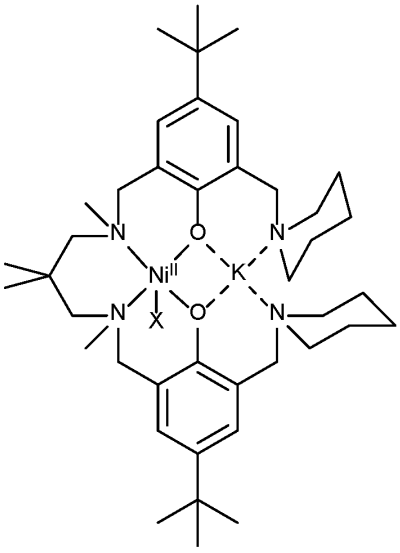
X=OAc



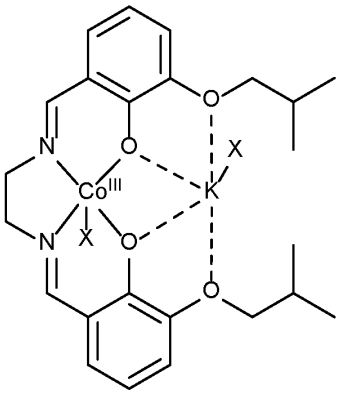
X=OAc



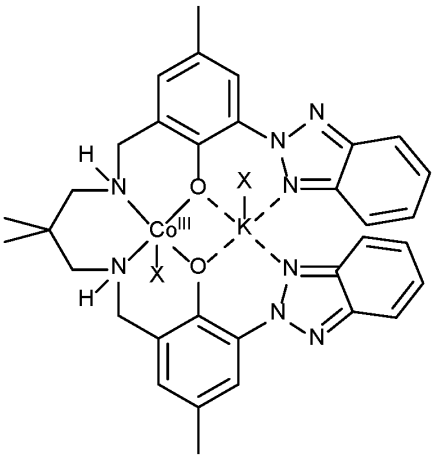
X=OAc, or OMe



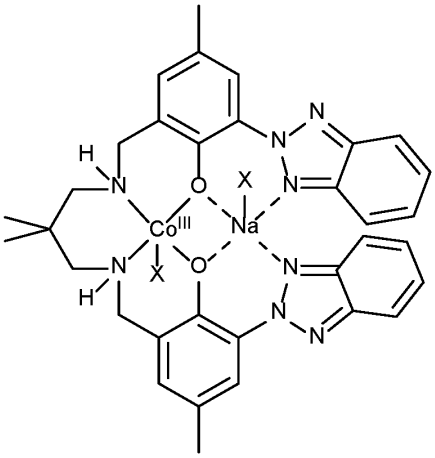
X=OAc



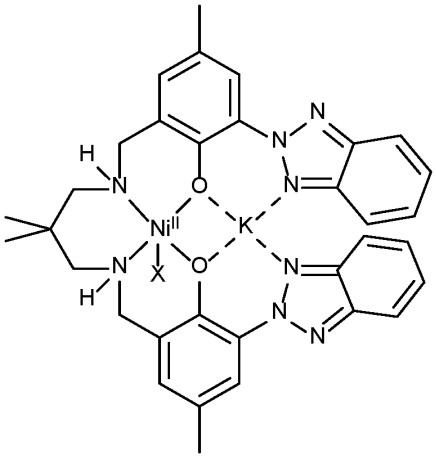
X=OAc



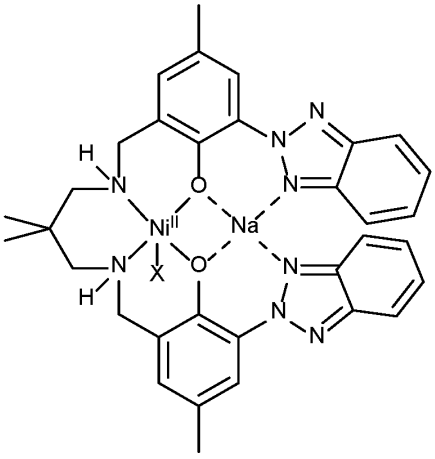
X=OAc or Cl



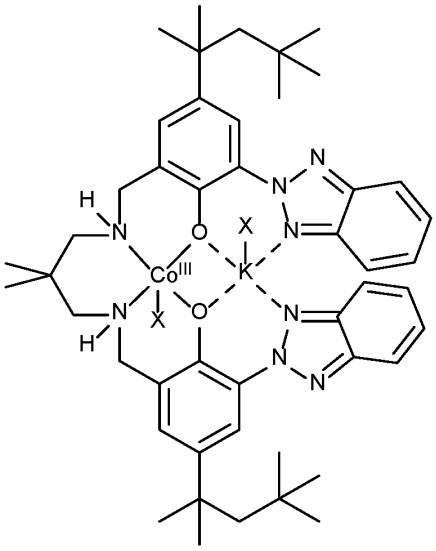
X=OAc



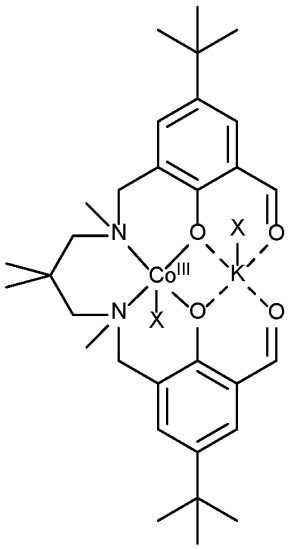
X=OAc



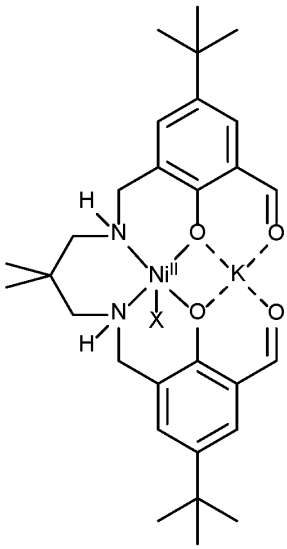
X=OAc



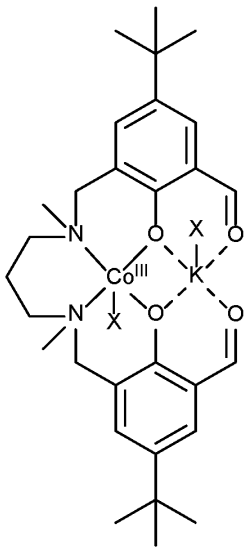
X=OAc



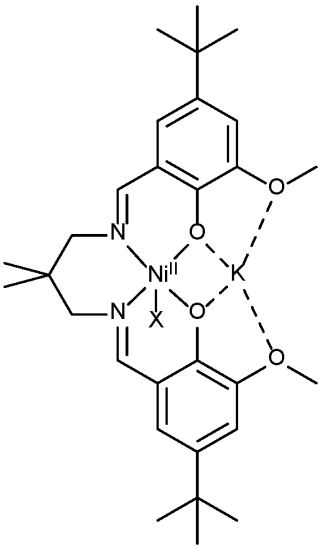
X=OAc



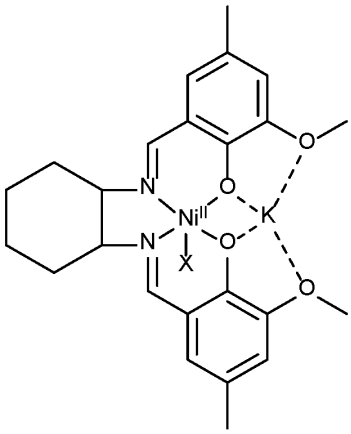
X=OAc



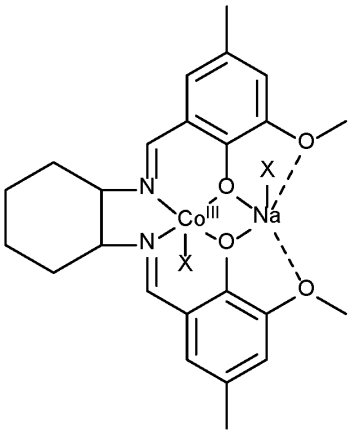
X=OAc



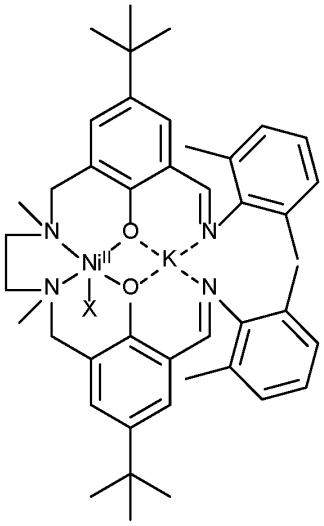
X=OAc



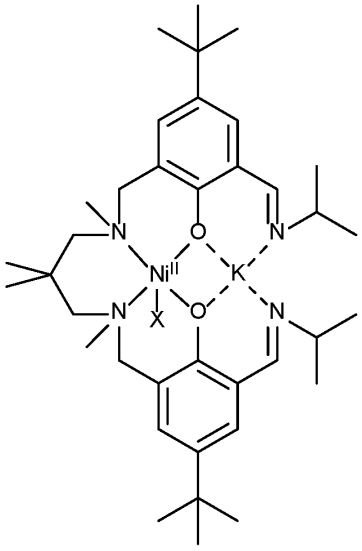
X=OAc, OMe or Cl



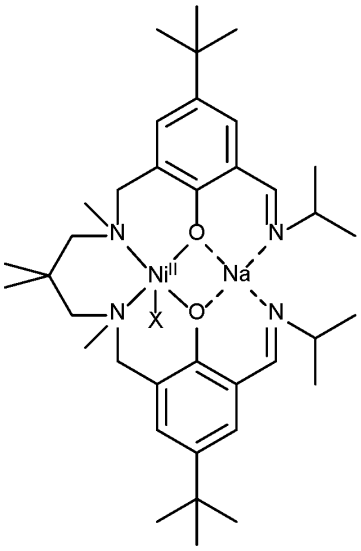
X=OAc



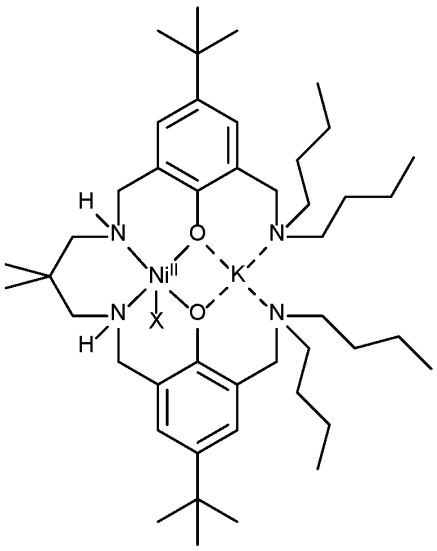
X=OAc



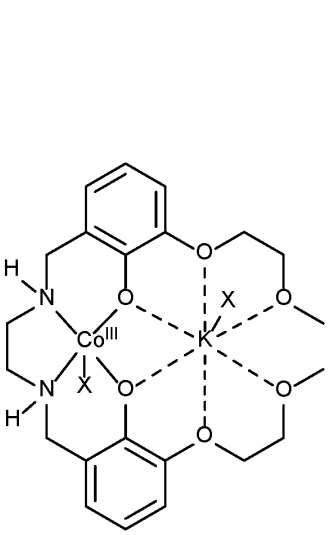
X=OAc



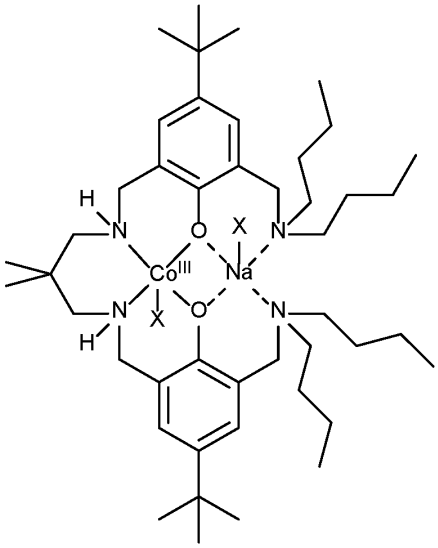
X=OAc or Cl



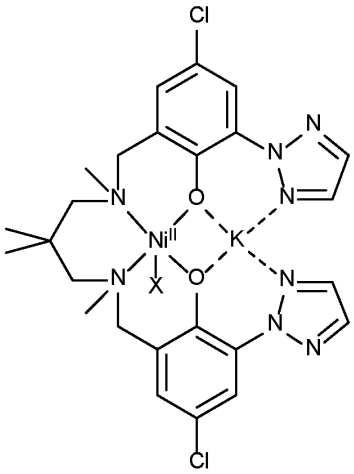
X=OAc



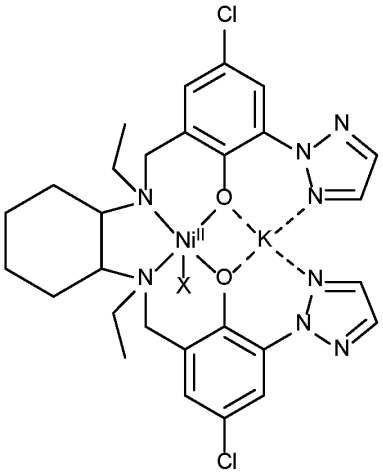
X=OAc



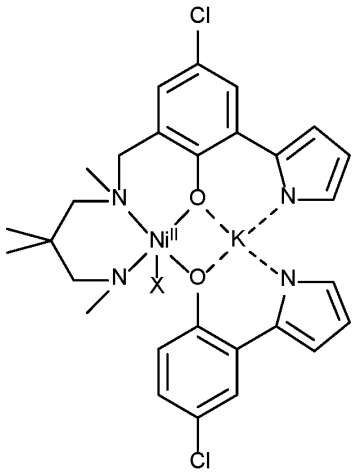
X=OAc



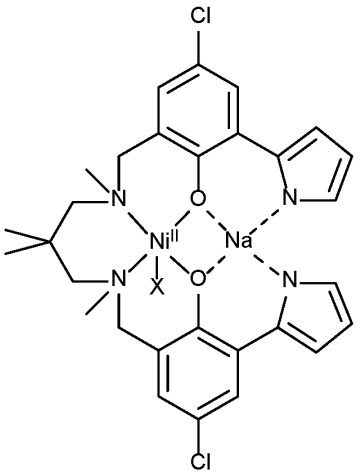
X=OAc, OPr or OCOOEt



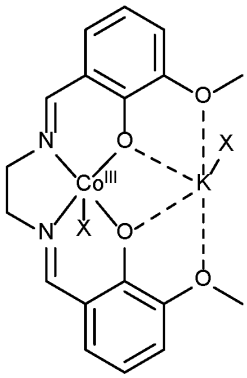
X=OAc



X=OAc or OEt

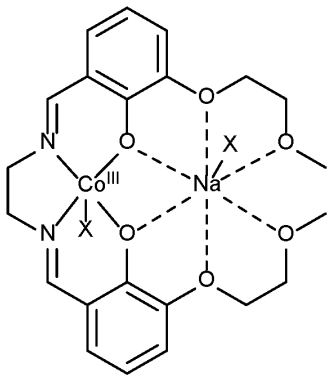


X=OAc



X=OAc or Cl

, or



X=OAc, OMe or OCOOMe

It will be apparent that X may alternatively be selected from a variety of compatible functional groups such as halide, alkoxy, sulphonate, phosphate, carboxylate, for example.

Co-catalyst (ether catalyst)

When the co-catalyst is an ether catalyst, the ether catalyst may be any catalyst suitable for polymerising epoxides to form polyethers. Suitable ether catalysts include DMC catalysts, metal alkoxides, boron-based catalysts such as BF_3 or BH_3, anionic catalysts such as KOH, cationic, acidic or superacidic catalysts (such as $HSbF_6$, CF_3SO_3H), PF_5, activated monomer catalysts, organic catalysts such as imidazole or phosphazene reagents and metallosalenate catalysts. Preferably the ether

catalyst is a DMC catalyst. Suitable DMC catalysts and their use are described in our WO2019048878, the contents of which are hereby incorporated by reference.

Starter compound

Suitable starter compounds (also known as chain transfer agents) are described in our WO2019048878, the contents of which are hereby incorporated by reference.

For example, the starter compound may be of the formula (III):

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

wherein:

Z can be any group which can have 2 or more $-R^Z$ groups attached to it. Thus, Z may be 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, for example Z may be an alkylarylene, heteroalkylarylene, heteroalkylheteroarylene or alkylheteroarylene group;

each R^Z may be –OH, -NHR', –SH, -C(O)OH, -P(O)(OR')(OH), -PR'(O)$(OH)_2$ or –PR'(O)OH, and R' may be H, or optionally substituted alkyl, heteroalkyl, aryl, heteroaryl, cycloalkyl or heterocycloalkyl; and

a is an integer which is at least 2.

In some preferred embodiments, the starter compound comprises a monofunctional starter compound.

Monohydric and polyhydric alcohols, including diols and triols, including polyalkylene glycols, are especially preferred starter compounds.

Reactants

When the polymerisation process of the present invention comprises the reaction of carbon dioxide with an epoxide and/or the reaction of an anhydride with an epoxide, the carbon dioxide may be

obtained from any source. Preferably, the carbon dioxide is obtained from waste industrial processes. Advantageously, using waste carbon dioxide emitted in industrial processes for the production of polymers enables the sequestration of undesirable carbon dioxide in the atmosphere, which reduces greenhouse gas emissions and fossil fuel consumption, especially compared to currently used petrochemicals.

When the polymerisation process of the present invention comprises the reaction of carbon dioxide with an epoxide and/or the reaction of an anhydride with an epoxide, the epoxide may be any compound comprising an epoxide moiety.

The epoxide may be aliphatic, cycloaliphatic, or aromatic. Examples of epoxides which may be used in the present invention include, but are not limited to, those disclosed in WO2020049319A1, the contents of which are hereby incorporated by reference.

It will be understood that the term "an epoxide" or "an alkylene oxide" is intended to encompass one or more epoxides. In other words, the term "an epoxide" or "an alkylene oxide" refers to a single epoxide, or a mixture of two or more different epoxides. For example, the epoxide substrate may be a mixture of ethylene oxide and propylene oxide, a mixture of cyclohexene oxide and propylene oxide, a mixture of ethylene oxide and cyclohexene oxide, or a mixture of ethylene oxide, propylene oxide and cyclohexene oxide.

Preferably, in a process of the invention for the manufacture of polycarbonate polyols, the epoxide is not solely propylene oxide, or is absent polypropylene oxide. Preferably in this case the epoxide comprises ethylene oxide. Advantageously, when the epoxide is not solely propylene oxide, and is selected from a range of epoxides, the properties of the polycarbonate polyols may be controlled for different applications. As mentioned above, ethylene oxide is preferred, giving rise to enhanced performance in certain applications (e.g. surfactants) and provides the polymer with a higher renewable (i.e. – CO_2 – derived) carbon content than would be the case with higher epoxides, including propylene oxide.

Preferably, the epoxide is aliphatic. Preferably, the epoxide is a C_1-C_{10} alkyl oxide. More preferably, the epoxide is ethylene oxide, propylene oxide, butylene oxide or a combination thereof. Most preferably, the epoxide is ethylene oxide, propylene oxide or a combination thereof. In some preferred embodiments, the epoxide is ethylene oxide.

When the polymerisation process of the fifth aspect of the present invention comprises the reaction of an anhydride with an epoxide, the anhydride may be any compound comprising an anhydride moiety in a ring system (i.e. a cyclic anhydride). The epoxide may be any of the epoxides described above.

Reaction Conditions

The polymerisation process may comprise the steps of (i) reacting a carbon dioxide with an alkylene oxide in the presence of a carbonate catalyst and, optionally, a starter compound (mono- or polyfunctional) to form a polycarbonate compound and (ii) reaction of the polycarbonate compound of step (i) with an alkylene oxide and a co-catalyst (e.g. an ether catalyst) to produce the polymer product.

The polymerisation process may be carried out in a single reaction zone in which CO_2 is contacted with an alkylene oxide in the presence of a catalyst of formula (I) and a co-catalyst, optionally also a solvent.

The polymerisation process may alternatively be carried out in a multiple reactor system; the system comprising a first and second reactor wherein a first reaction takes place in the first reactor and a second reaction takes place in the second reactor; wherein the first reaction is the reaction of a carbonate catalyst with CO_2 and an alkylene oxide, in the presence of a starter compound, and optionally a solvent, to produce a polycarbonate compound and the second reaction is the semi-batch or continuous reaction of an ether catalyst with the polycarbonate compound of the first reaction and an alkylene oxide to produce the polymer product.

Having the reactions with the two different catalysts separate and mixing only certain components in the first reaction and adding the remainder in the second reaction may also be useful, for example by adding a pre-activated ether catalyst or adding the reaction mixture to a pre-activated ether catalyst.

The polymerisation process of the present invention may be carried out at any suitable pressure.

The polymerisation process may be carried out at a pressure of 1 to 100 atmospheres, preferably at 1 to 40 atmospheres, such as at 1 to 20 atmospheres, more preferably at 1 or 10 atmospheres.

Advantageously, the catalysts of formula (I) used in the polymerisation process allow the reaction to be carried out at lower pressures relative to conventional catalysts in the art. For example, the catalysts of formula (I) may allow the reaction to be carried out at low pressure such as 1 atmosphere. However, for the avoidance of doubt, the catalysts of formula (I) are also active at much higher pressures, such as 40 atmospheres.

The polymerisation process may be carried out at any suitable temperature. The polymerisation process may be carried out at a temperature of about 0ºC to about 250ºC, preferably from about 40°C to about 160°C, even more preferably from about 50˚C to about 120˚C. Advantageously, the catalysts of formula (I) used in the polymerisation process allow the reaction to be carried out at lower temperatures relative to conventional catalysts in the art.

When the polymerisation process comprises the reaction of carbon dioxide with an epoxide, the process temperature (i.e. the temperature at which the polymerisation process is carried out) may be used to control the product composition.

The polymerisation process may be carried out at low catalytic loading. For example, when the polymerisation comprises the reaction of carbon dioxide with an epoxide, the catalytic loading for the process is preferably about 1:1,000-100,000 catalyst:epoxide, more preferably about 1:1,000-300,000 catalyst:epoxide, even more preferably about 1:10,000-100,000, and most preferably about 1:50,000-100,000 catalyst:epoxide. When the polymerisation process comprises the reaction of an anhydride with an epoxide the catalytic loading for the process is preferably about 1:1,000-300,000 catalyst:total monomer content, more preferably about 1:10,000-100,000 catalyst:total monomer content, most preferably about 1:50,000-100,000 catalyst:total monomer content. For the avoidance of doubt, the ratios above are molar ratios.

The polymerisation process may be carried out in the presence of a solvent. Examples of solvents useful in this aspect include ethyl acetate, propyl acetate, butyl acetate, acetone, toluene, diethyl carbonate, dimethyl carbonate, dioxane, dichlorobenzene, methylene chloride, propylene carbonate, ethylene carbonate, etc, or any other suitable green solvent.

The polymerisation process can be carried out in a batch reactor or a continuous reactor.

The polymerisation process may be carried out in a one pot reactor or may be a dual reactor process.

The term “continuous” used herein can be defined as the mode of addition of materials or may refer to the nature of the reaction method as a whole.

In terms of continuous mode of addition, the relevant materials are continually or constantly added during the course of a reaction. This may be achieved by, for example, adding a stream of material with either a constant flow rate or with a variable flow rate. In other words, the one or more materials are added in an essentially non-stop fashion. It is noted, however, that non-stop addition of the materials may need to be briefly interrupted for practical considerations, for example to refill or replace a container of the materials from which these materials are being added.

In terms of a whole reaction being continuous, the reaction may be conducted over a long period of time, such as a number of days, weeks, months, etc. In such a continuous reaction, reaction materials may be continually topped-up and/or products of the reaction may be tapped-off. It will be appreciated that although catalysts may not be consumed during a reaction, catalysts may in any case require topping-up, since tapping-off may deplete the amount of catalyst present.

A continuous reaction may employ continuous addition of materials.

A continuous reaction may employ a discontinuous (i.e., batch-wise or semi batch-wise) addition of materials.

Adding the components in separate steps may be useful to increase activity of the catalysts and may lead to a more efficient process, compared with a process in which all of the materials are provided at the start of the process. Large amounts of some of the components present throughout the process may reduce efficiency of the catalysts. Reacting this material in separate steps may prevent this reduced efficiency of the catalysts and/or may optimise catalyst activity. The reaction conditions of each step can be tailored to optimise the reactions for each catalyst.

In embodiments where two reactors are employed, the two reactors may be located in a series, or the reactors may be nested. Each reactor may individually be a stirred tank reactor, a loop reactor, a tube reactor, or other standard reactor design.

The term series used herein refers to when two or more reactors are connected so that the crude reaction mixture can flow from the first reactor to the second reactor. Preferably, the second reactor is run in a continuous mode.

The product of the first reaction may be stored for subsequent later use in the second reactor.

The term nested used herein refers to when two or more reactors are configured so that one is located within the other. For example, in the present invention, when the second reactor is located inside the first reactor, allowing the conditions of both reactors to influence the other.

Products

The polymer products of the polymerisation process the present invention may be polymers containing carbonate linkages, for example copolymers (block or random) containing carbonate linkages. Such polymers may for example include polycarbonates, polycarbonate ethers, polyether carbonates, polycarbonate ether polyols, polyether carbonate polyols, polyether polyols, polycarbonate polyols and polyester polyols.

It will be appreciated by the skilled person that when the polymerisation process of the invention comprises the reaction of carbon dioxide with an epoxide, the polymer product may be a polycarbonate or a polyether carbonate polyol. When the polymerisation process comprises the reaction of an anhydride with an epoxide the polymer product is a polyester polyol.

The polymer products may have any suitable number-average molecular weight (Mn). Preferably, the number-average molecular weight (M_n) of the polymer products may be from about 250 g/mol, from about 500 g/mol or from about 1,000 g/mol to about 100,000 g/mol. The number-average molecular weight (Mn) of the polymer products may be measured by Gel Permeation Chromatography (GPC) using, for example, a GPC-60 manufactured by Polymer Labs, using THF as the eluent at a flow rate of 1 ml/min on Mixed B columns, manufactured by Polymer Labs. Narrow molecular weight polystyrene standards can be used to calibrate the instrument.

A starter compound may be used to control the molecular weight (M_n) of the polymer products. For example, it is possible to produce polymers or polyether carbonate polyols and polyester polyols

having a M_n of from about 200 g/mol to about 20,000 g/mol, preferably less than about 10,000 g/mol by adding a starter compound to the polymerisation process.

The polymer products may have a polydispersity index (PDI) of less than about 2, preferably less than about 1.5, even more preferably less than about 1.2. Advantageously, it is possible to control the molecular weight distribution so as to produce multi-modal or broad molecular weight distribution polymers by the addition of one or more starter compound(s).

The polymer products may be useful building blocks in the preparation of various copolymeric materials.

The polymer products may undergo further reaction, for example to produce a higher polymer such as polyurethanes, polyureas or polyamines. These processes and reactions would be well known to the skilled person (for example, refer to WO2013/034750).

The polymer products of the invention may find various application, including (but not limited to) adhesives (such as hot melt adhesives and structural adhesives), binders (such as forest product binders, foundry core binders and rubber crumb binders), coatings (such as powder coatings, transport, e.g. automotive or marine coatings, fast cure coatings, self-healing coatings, top coats and primers, varnishes, and coatings for marine applications, e.g. oil rigs), elastomers (such as cast elastomers, fibres/spandex elastomers, footwear elastomers, RIM/RRIM elastomers, synthetic leather elastomers, technical microcellular elastomers and TPU elastomers), flexible foams (such as viscoelastic foams), rigid foams (such as rigid and flexible panels, moulded rigid foams, aerosol gap filling foam, spray foams, refrigeration foams, pour-in-place foams, and foam slabs) and sealants (such as glazing sealants for commercial, industrial and transport (e.g. automotive) applications, and construction sealants). Polyamines and polyureas can be processed using methods standard techniques known in the art, such as foaming.

It will be understood that the polyols produced by the polymerisation process of the invention may be mixed with other polyols prior to further use or reaction.

Polymers according to the invention may have a number of beneficial properties including high strength, high toughness, high gloss, high transparency, low haze, high gas (e.g. oxygen and carbon dioxide) or water barrier properties, flame resistance, UV resistance, high durability, rigidity and

stiffness, compatibility with plasticizers, broad dimensional stability temperature, biodegradability and biocompatibility, and modulus of elasticity and yield strength comparable to LDPE. Thus, these polymers may be used in various applications and products, such as electronic components, construction materials, data storage products, automotive and aircraft products, security components, medical applications, mobile phones, packaging (including bottles), optical applications (such as safety glass, windscreens, etc).

Surfactants

The invention provides a process for producing a surfactant comprising reacting carbon dioxide and an epoxide in the presence of a double metal cyanide (DMC) catalyst, a catalyst of formula (I), and a functional starter compound to produce a surfactant, as aforesaid.

The process for producing the surfactant may be carried out in a multiple reactor system; the system comprising a first and second reactor wherein a first reaction takes place in the first reactor and a second reaction takes place in the second reactor; wherein the first reaction is the reaction of a carbonate catalyst with CO_2 and epoxide, in the presence of a monofunctional starter compound, and optionally a solvent, to produce a polycarbonate compound and the second reaction is the semi-batch or continuous reaction of an ether catalyst with the polycarbonate compound of the first reaction and epoxide to produce the surfactant.

Preferably, the surfactant has a molecular weight (Mn) in the range of from about 300 to 20,000 Da, more preferably in the range of from about 400 to 8000 Da, most preferably from about 500-6000 Da.

The surfactant may comprise a polycarbonate block and a polyether block.

The polycarbonate block of the surfactant may preferably have a molecular weight (Mn) in the range of from about 200 to 4000 Da, more preferably in the range of from about 200 to 2000 Da, most preferably from about 200 to 1000 Da, especially from about 400 to 800 Da.

The polyether block of the surfactant may preferably have a molecular weight (Mn) in the range of from about 100 to 20,000 Da, more preferably of from about 200 to 10,000 Da, most preferably from about 200 to 5000 Da.

Also provided in accordance with the invention is the use of the aforesaid surfactants: in home and personal care products; in industrial and institutional cleaning agents; as agrichemical adjuvants; for the preparation of foams, coatings, paints, adhesives and sealants for the building construction industry; in the automotive industry; in the manufacture of textiles; for the enhanced recovery of crude oil.

All of the features contained herein may be combined with any of the above aspects and in any combination.

Embodiments of the invention will now be described with reference to the following non-limiting examples.

EXAMPLES

Synthesis of Catalyst

Cat1 Synthesis

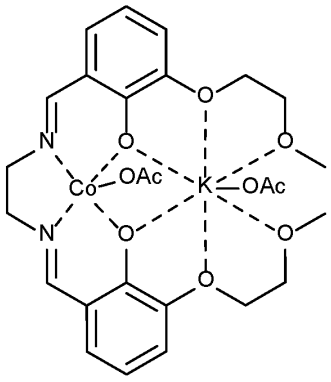
A catalyst in accordance with the present invention was prepared according to modified procedures presented in *J. Am. Chem. Soc.*, 1993, 115 (14), 5962-5969 and *J. Am. Chem. Soc.*, 2020, 142 (45), 19150-19160.

The modified procedure involved the following steps.

Step 1: 2,3-Dihydroxybenzaldehyde (12 g) in DMSO was added slowly to NaH (7.5 g) in degassed DMSO at 0 °C and the reaction warmed to room temperature. 2-Methoxyethyl p-toluenesulfate (22 g) was added dropwise and the mixture stirred for 16 hours. After quenching the reaction, the product was extracted into $CHCl_3$ and washed with 1 M HCl (10 g).

Step 2: Ethylenediamine (1.6 g) in MeOH was added to the product from Step 1 (10 g) in MeOH and the mixture stirred for 6 hours. The ligand was isolated by evaporation (10 g).

Step 3: The ligand from Step 2 (10 g), KOAc (2.5 g) and $Co(OAc)_2 \cdot 4H_2O$ (6.4 g) were dissolved in dry MeCN (100 mL) and stirred under N_2 at room temperature for 16 hours. Solvent was removed by evaporation and the crude product washed with ether to yield Cat1 (quant.).



Cat1

Cat2 Synthesis

As per the procedure for Cat1, with the product of Step 1 replaced with o-vanillin.

Cat3 Synthesis

As per the procedure for Cat1, with KOAc replaced with NaOAc.

Cat4 Synthesis

As per the procedure for Cat1, with ethylenediamine replaced with cyclohexanediamine.

Cat5 Synthesis

As per the procedure for Cat1, with 2,3-dihydroxy-5-^{t}butyl-benzaldehyde.

Cat6 Synthesis

As per the procedure for Cat1, with ethylenediamine replaced with phenylene-1,2-diamine.

Cat7 Synthesis

As per the procedure for Cat1, with 2-methoxyethyl p-toluenesulfate replaced with 2-isobutyl-4-tosylate.

The general structure for Cat2 to Cat7 is shown below.

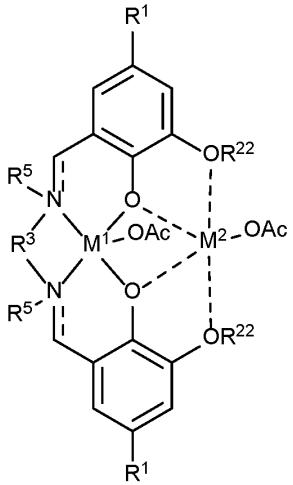


Table 1 provides details of the different substituent groups in each of Cat2 to Cat7.

Table 1

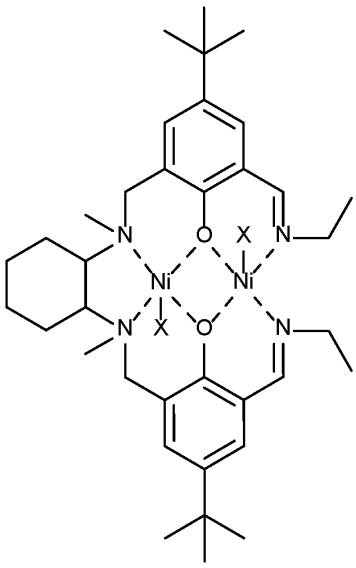
	R^1	R^3	R^5	R^{22}	M^1	M^2	
Cat2	H	CH_2CH_2	Absent	Me	Co	K	
Cat3	H	CH_2CH_2	Absent	CH_2CH_2OMe	Co	Na	
Cat4	H	C_6H_{10}	Absent	CH_2CH_2OMe	Co	K	
Cat5	^{t}Bu	CH_2CH_2	Absent	CH_2CH_2OMe	Co	K	
Cat6	H	C_6H_6	Absent	CH_2CH_2OMe	Co	K	
Cat7	H	CH_2CH_2	Absent	CH_2CHMe_2	Co	K	

- For Cat2 to Cat7, R^2 and R^4 groups are all H

Catalyst Performance

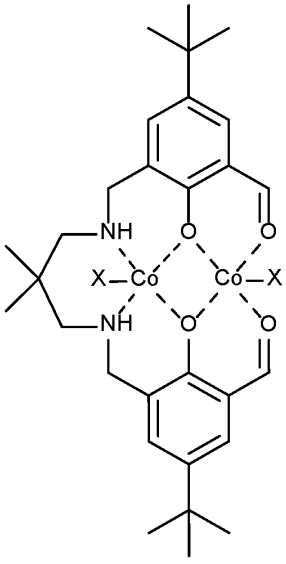
Catalysts Cat1 to Cat7 and comparative catalysts involving only transition metals were used in a ring-opening copolymerization reaction of epoxide (propylene oxide (PO) or ethylene oxide (EO)) and CO_2 at a range of temperatures and pressures, as detailed in Table 2.

The comparative catalyst used in Examples 1-3 had the following structure:



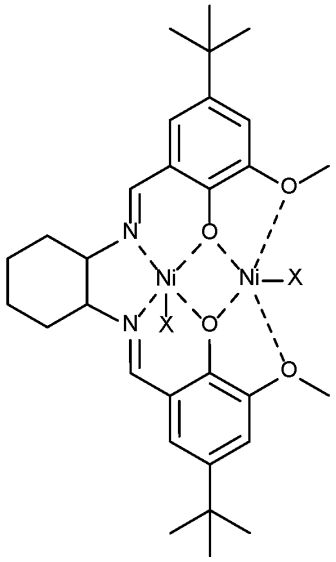
X = OAc

The comparative catalyst used in Example 6 had the following structure:



X = OAc

The comparative catalyst used in Example 7 had the following structure:



X = OAc

Table 2

Catalyst performance experimental conditions; results

Example	Catalyst	Cat Type + Metal	Cat / g	Starter	PO / mL	EO / mL	Temp / °C	Pressure / barg	Time / h	Conv / %	Select / %	Mn	PDI
1	Comp	Transition	0.07	Dodecanol	15	0	75	20	16	18	35	520	1.09
2	Comp	Transition	0.07	Dodecanol	15	0	75	20	16	17	47	700	1.12
3	Comp	Transition	0.07	Dodecanol	15	0	65	20	16	4	64	50	1.08
4	Cat1	Transition/Alkali	0.10	Hexanol	50	0	70	20	5	62	40	500	1.10
5	Cat1	Transition/Alkali	0.10	Dodecanol	40	0	60	20	16	67	74	1140	1.13
6	Comp	Transition	0.07	Dodecanol	15	0	65	20	16	NR	NR	NR	NR
7	Comp	Transition	0.07	Dodecanol	15	0	75	20	16	NR	NR	NR	NR
8	Cat1	Transition/Alkali	0.27	EtOH	40	0	50	20	6	82	98	760	1.12
9	Cat1	Transition/Alkali	0.12	EtOH	40	0	50	20	10	81	97	740	1.11
10	Cat1	Transition/Alkali	0.10	EtOH	40	0	45	20	16	79	99	730	1.11
11	Cat1	Transition/Alkali	0.71	Hexanol	0	120	50	20	16	80	90	1200	1.08

12	Cat2	Transition/Alkali	0.12	EtOH	40	0	50	20	16	68	96	1300	1.09
13	Cat3	Transition/Alkali	0.12	EtOH	40	0	50	20	16	64	97	720	1.09
14	Cat4	Transition/Alkali	0.12	EtOH	40	0	50	20	16	72	91	1170	1.07
15	Cat5	Transition/Alkali	0.12	EtOH	40	0	50	20	16	64	96	1000	1.07
16	Cat6	Transition/Alkali	0.12	EtOH	40	0	50	20	16	50	93	800	1.09
17	Cat7	Transition/Alkali	0.12	EtOH	40	0	50	20	16	14	80	300	1.08

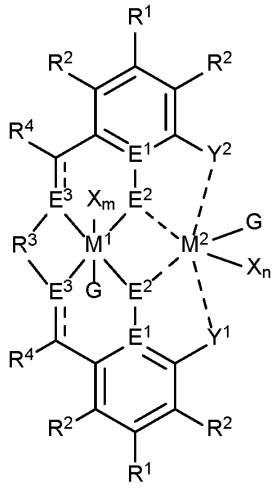
NR = no reaction

WO 2025/176881 PCT/EP2025/054795

The data in Table 2 demonstrates that by providing the catalyst in the open form with a transition metal/alkali metal combination, enhanced reaction rates and selectivity for the polymer product can be achieved at comparative temperatures and pressures to those achieved by equivalent catalysts comprising two transition metal/main block metal centres.

CLAIMS

1. A bimetallic heterodinuclear catalyst of formula (I):



Formula (I)

wherein R^1 and R^2 are independently selected from hydrogen, halide, a nitro group, a nitrile group, an imine group, -$NCR^{13}R^{14}$, an amine, an ether –OR^{15}, –$R^{16}OR^{17}$, an ester group –$OC(O)R^{10}$ or –$C(O)OR^{10}$, an amido group –$NR^9C(O)R^9$ or –$C(O)$-$NR^9(R^9)$, -COOH, -$C(O)R^{15}$, –$OP(O)(OR^{18})(OR^{19})$,–$P(O)R^{20}R^{21}$, -P(O)(OR)(OR), -OP(O)R(OR), 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^4 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

R^9, R^{10}, R^{13}, R^{14}, R^{18}, R^{19}, R^{20} and R^{21} are independently selected from hydrogen or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group;

E^1 is C, E^2 is O, S or NH or E^1 is N and E^2 is O;

E^3 is N, NR^5, O or S, wherein when E^3 is N, ------ is ═══, and when E^3 is NR^5, O or S, ------ is ———;

R^5 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl, -alkylC(O)OR^{10}, -alkylnitrile, 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, nitro, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl;

m and n are integers between 0-3, such that the sum of m and n is between 0-4

R^x is independently selected from hydrogen or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group;

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

Y^1 and Y^2 are independently a neutral or anionic donor groups capable of donating at least one lone pair to the metal M^2 selected from a group with the at least one lone pair donated by a nitrogen atom (aromatic or non-aromatic), a group with the at least one lone pair donated by a carbene carbon atom, a group with the at least one lone pair donated by an ether group oxygen atom, a group with the at least one lone pair donated by a carbonyl oxygen atom and a group with the at least one lone pair donated by a carboxylate oxygen atom; and

at least one of M^1 and M^2 is an alkali or alkaline earth metal.

2. The catalyst according to Claim 1 wherein M^1 and M^2 are independently selected from transition and/or main block metals and/or alkali or alkaline earth metals, wherein when M^1 is a transition and/or main block metal, M^2 is an alkali or alkaline earth metal, or wherein when M^1 is an alkali or an alkaline earth metal, M^2 is a transition and/or main block metal.

3. The catalyst according to Claim 2, wherein when one of M^1 and M^2 is Mg, the other of M^1 and M^2 is not a transition metal or main block metal.

4. The catalyst according to either one of Claims 2 or 3, wherein M^1 is a transition metal or main block metal, whilst M^2 is an alkali or alkaline earth metal.

5. The catalyst according to any one of Claims 2 to 4, wherein when M^1 or M^2 is a transition and/or main block metal, the transition and/or main block metal is selected from Zn(II), Cr(II), Co(II), Cu(II), Mn(II), Ni(II), Fe(II), Ti(II), V(II), Cr(III), Co(III), Mn(III), Ni(III), Fe(III), Ge(II), Al(III),

Ti(III), V(III), Ge(IV), Y(III), Sc(III) or Ti(IV), optionally from Co(III), Ni(II), Fe(II), Fe(III), Al(III), Co(II), Cr(III) or Zn(II)

6. The catalyst according to any one of Claims 1 to 5, wherein when M^1 or M^2 is an alkali or alkaline earth metal, the alkali or alkaline earth metal is selected from Li(I), Na(I), K(I), Rb(I), Cs(I), Fr(I), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Ra(II).

7. The catalyst according to Claim 6, wherein when M^1 or M^2 is an alkali or alkaline earth metal, the alkali or alkaline earth metal centre is K(I) or Na(I).

8. The catalyst according to any one of Claims 1 to 7, wherein Y^1 and Y^2 are each independently selected from a group wherein the or each lone pair is donated by an ether group oxygen atom, optionally wherein Y^1 and Y^2 are each an ether chain comprising more than one oxygen atom, each oxygen atom donating a lone pair to the metal centre.

9. The catalyst according to claim 8 wherein Y^1 Y^2 are each independently selected from O, -OCH_3, -OCH_2CH_3, -$OCH_2CH_2CH_3$, -$OCH_2CH(CH_3)_2$, -C(=O)H, or from ethers, including -OCH_2CH_2OMe, -OCH_2CH_2OPh, -OCH_2CH_2OiPr, -OCH_2CH_2OEt, -OCH_2CH_2OnBu.

10. The catalyst according to any one of Claims 1 to 7, wherein Y^1 and Y^2 are each independently selected from amines, including -$CH_2N(CH_3)_2$, -$CH_2N(H)(CH_2CH(CH_3)_2)$, -$CH_=N(CH_2CH(CH_3)_2)$, -CH_2-piperidine or benzotriazine.

11. A polymer produced using the bimetallic heterodinuclear catalyst according to any one of Claims 1 to 10.

12. The polymer according to Claim 11, wherein the polymer contains carbonate linkages, optionally wherein the polymer is selected from polycarbonates, polycarbonate ethers, polyether carbonates, polycarbonate ether polyols, polyether carbonate polyols, polyether polyols, polycarbonate polyols or polyester polyols.

13. The polymer according to Claim 11 or claim 12, wherein the polymer has the formula (II):

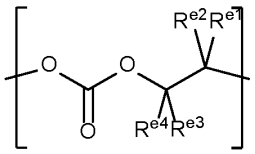
$$Z^1\text{-}((PC)_P\text{-}(PE)_Q\text{-}Z^2)_X \qquad (II)$$

wherein:

Z^1 is either derived from a starter compound or from X;

the or each Z^2 is independently an ionic species, or OH, O-R', O-C(O)-R' or O-C(O)-O-R', wherein R' is an optionally substituted hydrocarbyl or heterohydrocarbyl;

PC represents a carbonate block with P repeat units of formula:

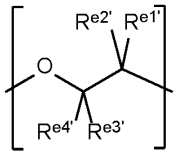


;

wherein:

R^{e1}, R^{e2}, R^{e3}, and R^{e4} are each independently selected from H, halogen, hydroxyl, or optionally substituted hydrocarbyl or heterohydrocarbyl;

PE represents a polyether block with Q repeat units of formula:



;

wherein:

$R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ are each independently selected from H, halogen, hydroxyl, or optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, heteroalkyl or heteroalkenyl;

wherein the value of the or each P is independently 1 or above;

wherein the value of the or each Q is independently 0 or above; and

X is 1 or more.

14. The polymer according to Claim 13, wherein when Z is derived from a starter compound, it is selected from R, R-O, R-C(O)-O or R-O-C(O)-O, wherein R is an optionally substituted hydrocarbyl or heterohydrocarbyl group, or R-NR'-, R–S-, , wherein R' is H, or an optionally substituted hydrocarbyl or heterohydrocarbyl group, or wherein Z is a phosphate, phosphinate, phosphonate, phosphite or hypophosphite derivative.

15. The polymer according to Claim 13, wherein when Z is derived from X, it is selected from R^x-C(O)-O, R^x-$S(O)_2$-O, R^x-S(O)-O, $(R^x)_2$-S(O)-O, $R^x(O)S$, R^x-O, phosphinate, halide, nitrate, hydroxyl, carbonate, amino, nitro, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl, and wherein R^x is selected from hydrogen or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group.

16. Use of a bimetallic heterodinuclear catalyst according to any one of Claims 1 to 10 in the manufacture of polymers.

17. Use of a bimetallic heterodinuclear catalyst according to any one of Claims 1 to 10 in the manufacture of polyols.

18. Use of a bimetallic heterodinuclear catalyst according to any one of Claims 1 to 10 in the manufacture of surfactants.

19. A process for producing a polymer comprising reacting carbon dioxide and an epoxide in the presence of a catalyst according to any one of Claims 1 to 10.

20. The process according to Claim 19 additionally comprising a starter compound, optionally wherein the starter compound facilitates the synthesis of polymers with defined molecular weights, structures, and end groups.

21. The process according to Claim 20, wherein the starter compound comprises a monofunctional starter compound.

22. The process according to any one of Claims 19 to 21, wherein the process further comprises a solvent, optionally wherein the solvent is selected from ethyl acetate, propyl acetate, butyl acetate, acetone, toluene, diethyl carbonate, dimethyl carbonate, dioxane, dichlorobenzene, methylene chloride, propylene carbonate or ethylene carbonate.

23. The process according to any one of Claims 19 to 22, wherein the process further comprises a co-catalyst, optionally wherein the co-catalyst is an ether catalyst.

24. The process according to any one of Claims 19 to 23, wherein the epoxide comprises at least one epoxide other than propylene oxide, optionally wherein the at least one epoxide comprises or consists of ethylene oxide.

25. A polymer produced by the process according to any one of Claims 19 to 24.

26. The polymer according to Claim 25, wherein the polymer is selected from a polyol or a surfactant.

27. A higher polymer produced using the polymer according to any one of Claims 25 or 26.

28. The higher polymer according to Claim 27, wherein the higher polymer is selected from a polyurethane, a polyurea or a polyamine.