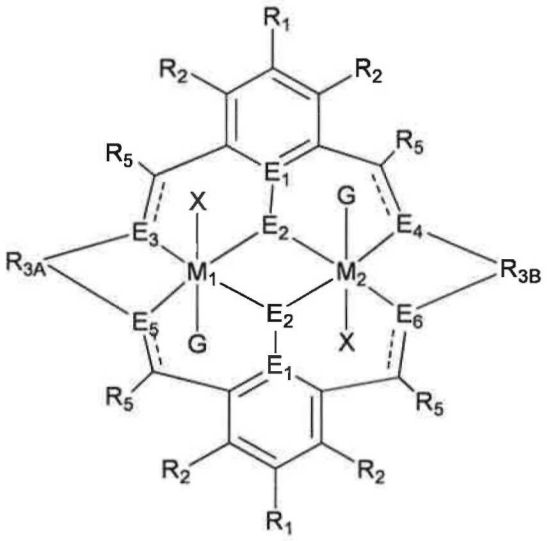
Claims

1. A catalyst of formula (I):



(I)

wherein:

M_1 and M_2 are independently selected from Zn(II), Cr(II), Co(II), Cu(II), Mn(II), Ni(II), Mg(II), Fe(II), Ti(II), V(II), Cr(III)-X, Co(III)-X, Ni(III)-X, Mn(III)-X, Fe(III)-X, Ca(II), Ge(II), Al(III)-X, Ti(III)-X, V(III)-X, Ge(IV)-$(X)_2$ or Ti(IV)-$(X)_2$;

R_1 and R_2 are independently selected from hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl group, a silyl ether group, a sulfoxide group, a sulfonyl group, a sulfinate group or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alkoxy, aryloxy, alkylthio, arylthio, alicyclic or heteroalicyclic group;

R_{3A} and R_{3B} are independently selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene, may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

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

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

E_3, E_4, E_5 and E_6 are each independently selected from N, NR_4, O and S, wherein when any of E_3, E_4, E_5 or E_6 are N, ------ is ═══, and wherein when any of E_3, E_4, E_5 or E_6 are NR_4, O or S, ------ is ———; R_4 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

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

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

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

and wherein:

i) at least one occurrence of E_3, E_4, E_5 and E_6 is different to a remaining occurrence of E_3, E_4, E_5 and E_6.

2. The catalyst of claim 1, wherein R_{3A} is the same as R_{3B} and at least one occurrence of E_3, E_4, E_5 and E_6 is different to a remaining occurrence of E_3, E_4, E_5 and E_6.

3. The catalyst of any preceding claim, wherein R_{3A} or R_{3B} is selected from substituted or unsubstituted alkylene, substituted or unsubstituted cycloalkylene or optionally substituted arylene, preferably substituted or unsubstituted propylene, substituted or unsubstituted cyclohexylene or substituted or unsubstituted phenylene or biphenylene, even more preferably ethylene, propylene, 2,2-dialkylpropylene such as 2,2-dimethylpropylene. 2,2-difluoropropylene, cyclohexylene or phenylene, even more preferably 2,2-dimethylpropylene.

4. The catalyst of any of claims 1, 2 or 3, wherein each E_3, E_4, E_5 and E_6 is NR_4, and one of the R_4 groups is different, preferably E_4 is different, preferably one of the R_4 groups is

selected from an optionally substituted alkyl or heteroalkyl, more preferably one of the R_4 groups is selected from methyl, ethyl, propyl, butyl or –alkyl- C(O)-OR_{19} such as methyl propanoate, preferably the remaining R_4 groups are hydrogen.

5. The catalyst of any of claims 1, 2 or 3, wherein each E_3, E_4, E_5 and E_6 is NR_4, and two of the R_4 groups are different, such as E_3 and E_5, E_3 and E_4, E_4 and E_6, E_4 and E_5, E_5 and E_6, and/or E_3 and E_6, preferably E_3 and E_6 or E_3 and E_5 are different, preferably two of the R_4 groups are selected from an optionally substituted alkyl or heteroalkyl, more preferably two of the R_4 groups are selected from methyl, ethyl, propyl, butyl or –alkyl-C(O)-OR_{19} such as methyl propanoate, preferably the remaining R_4 groups are hydrogen.

6. The catalyst of any preceding claim wherein M_1 or M_2 is selected from Mg(II), Ni(II), Ni(III)-X, Co(II), Co(III)-Xand Zn(II).

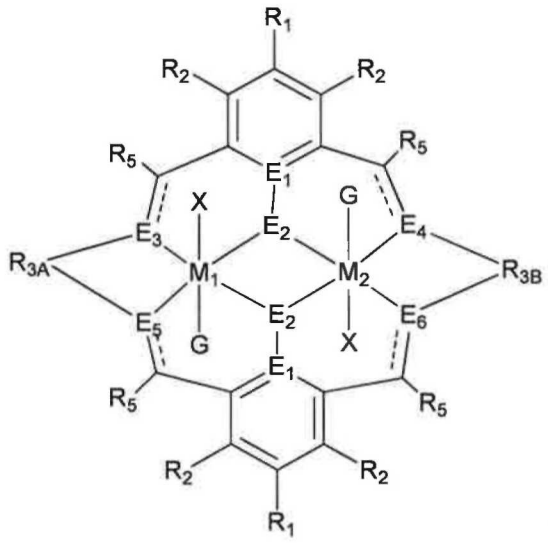
7. The catalyst of any of claims 1, 2, 3, 4 or 6 wherein M_1 and M_2 are the same and are Ni(II), and each E_3, E_4, E_5 and E_6 is NR_4, wherein at least one of the R_4 groups is different from a remaining occurrence of R_4 and is selected from an optionally substituted alkyl or heteroalkyl and preferably the remaining R_4 group/s are hydrogen.

8. The catalyst according to any preceding claim, wherein R_1 is independently selected from hydrogen, halide, amino, nitro, sulfoxide, sulfonyl, sulfinate, and optionally substituted alkyl, alkenyl, aryl, heteroaryl, alkoxy or alkylthio, preferably R_1 is an optionally substituted alkyl, more preferably R_1 is tertiary butyl.

9. The catalyst according to any preceding claim, wherein X is independently $OC(O)R^x$, $OSO2R^x$, $OS(O)R^x$, $OSO(R^x)2$, $S(O)R^x$, OR^x, halide, nitrate, hydroxyl, carbonate, amino, nitro, amido, and optionally substituted alkyl, heteroalkyl, aryl or heteroaryl, preferably X is $OC(O)R^x$, more preferably X is acetate, wherein preferably, R^x is independently optionally substituted alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl or alkylaryl.

10. The catalyst according to any of claims 1 or 3-9, wherein R_{3A} is different from R_{3B}.

11. A catalyst of formula (I):



(I)

wherein:

M_1 and M_2 are independently selected from Zn(II), Cr(II), Co(II), Cu(II), Mn(II), Ni(II), Mg(II), Fe(II), Ti(II), V(II), Cr(III)-X, Co(III)-X, Ni(III)-X, Mn(III)-X, Fe(III)-X, Ca(II), Ge(II), Al(III)-X, Ti(III)-X, V(III)-X, Ge(IV)-$(X)_2$ or Ti(IV)-$(X)_2$;

R_1 and R_2 are independently selected from hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl group, a silyl ether group, a sulfoxide group, a sulfonyl group, a sulfinate group or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alkoxy, aryloxy, alkylthio, arylthio, alicyclic or heteroalicyclic group;

R_{3A} and R_{3B} are independently selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene, may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

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

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

E_3, E_4, E_5 and E_6 are each independently selected from N, NR_4, O and S, wherein when any of E_3, E_4, E_5 or E_6 are N, ------ is ═══, and wherein when any of E_3, E_4, E_5 or E_6 are NR_4, O or S, ------ is ———; R_4 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

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

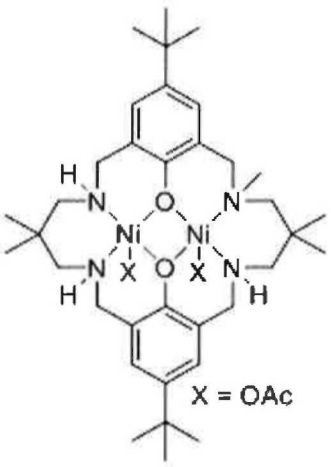
R_x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl; and

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

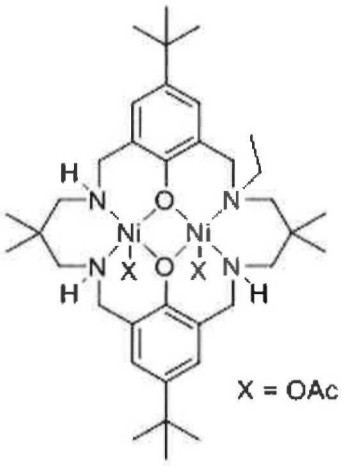
and wherein:

i) R_{3A} is different from R_{3B}; and/or

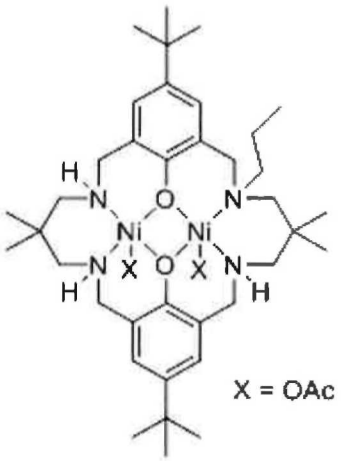
ii) at least one occurrence of E_3, E_4, E_5 and E_6 is different to a remaining occurrence of E_3, E_4, E_5 and E_6; and wherein the catalysts are selected from:-



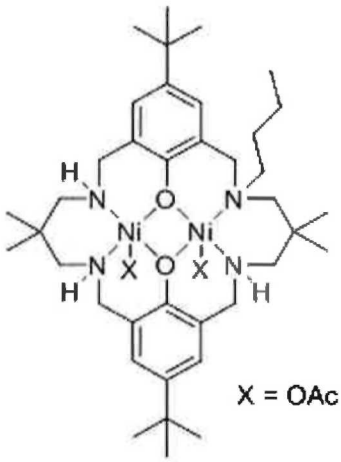
$L^1Ni_2(OAc)_2$



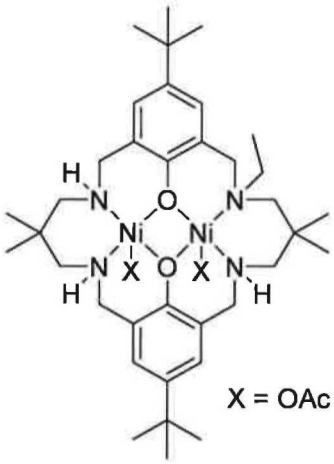
$L^2Ni_2(OAc)_2$



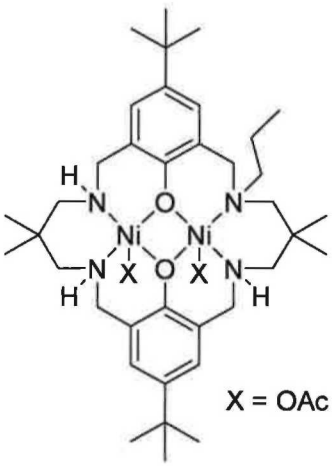
$L^3Ni_2(OAc)_2$



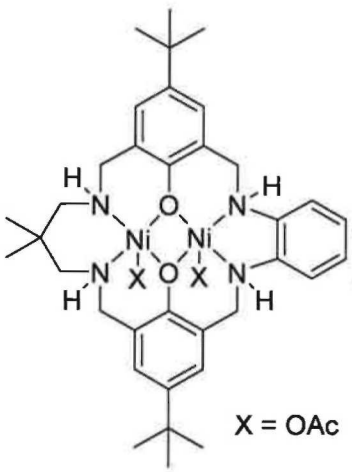
$L^4Ni_2(OAc)_2$



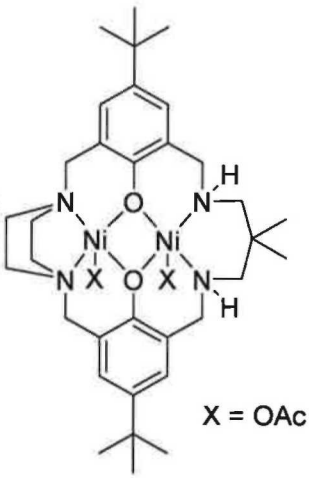
$L^2Zn_2(OAc)_2$



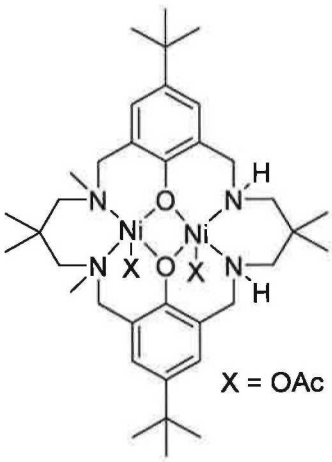
$L^3Mg_2(OAc)_2$



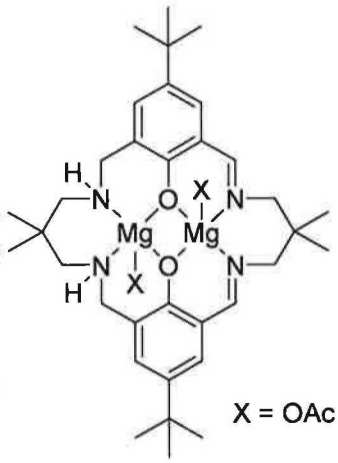
$L^5Ni_2(OAc)_2$



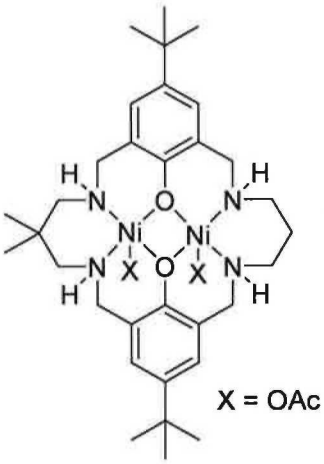
$L^6Ni_2(OAc)_2$



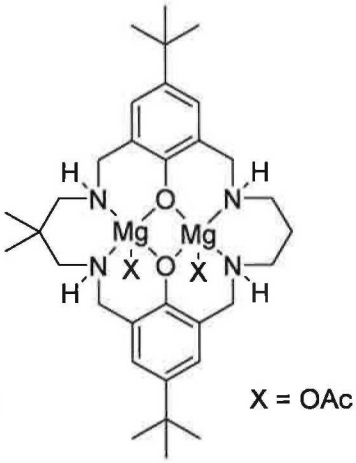
$L^7Ni_2(OAc)_2$



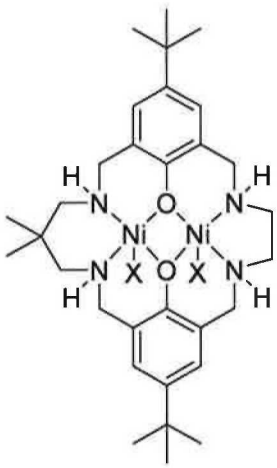
$[L_{imine}{}^8Mg_2(OAc_2)]$



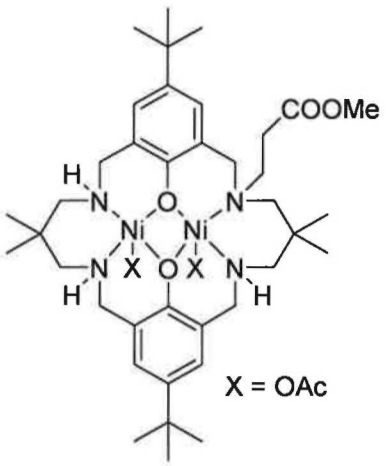
$L^9Ni_2(OAc)_2$



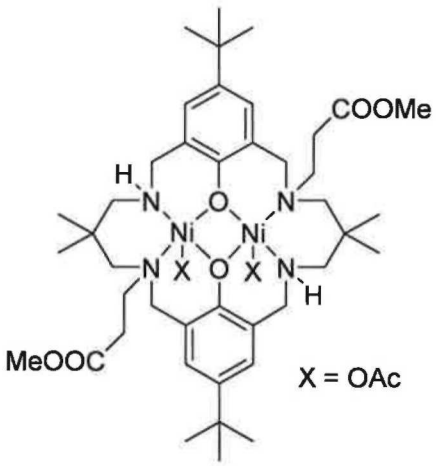
$L^9Mg_2(OAc)_2$



$L^{10}Ni_2(OAc)_2$

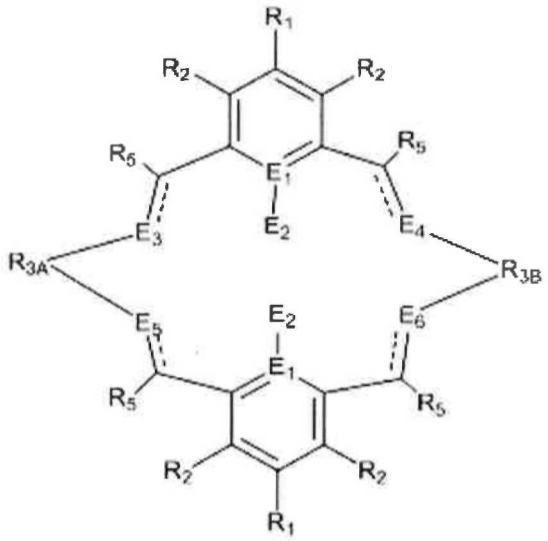


$L^{12}Ni_2(OAc)_2$



$L^{13}Ni_2(OAc)_2$

12. A ligand of formula (II):



(II)

wherein:

R_1 and R_2 are independently selected from hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl group, a silyl ether group, a sulfoxide group, a sulfonyl group, a sulfinate group or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alkoxy, aryloxy, alkylthio, arylthio, alicyclic or heteroalicyclic group;

R_{3A} and R_{3B} are independently selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or

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

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

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

Y is hydrogen or an alkali metal;

E_3, E_4, E_5 and E_6 are each independently selected from N, NR_4, O and S, wherein when any of E_3, E_4, E_5 or E_6 are N, ------is ═══, and wherein when any of E_3, E_4, E_5 or E_6 are NR_4, O or S, ------is ———; R_4 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

and wherein:

(i) at least one occurrence of E_3, E_4, E_5 and E_6 is different to a remaining occurrence of E_3, E_4, E_5 and E_6.

13. The ligand of claim 12, wherein the groups R_1, R_2, R_{3A}, R_{3B}, R_4, R_5, E_1, E_2, E_3, E_4, E_5, and E_6 are as defined in any of claims 2-10.

14. The ligand of claim 12 or 13, wherein R_{3A} is different from R_{3B}.

15. A process of asymmetric N-substitution of a symmetrical ligand having a tetraaminophenol coordination sphere, the process comprising the following steps:

a) protecting at least two of the amino groups of the coordination sphere of the symmetrical ligand with an optionally substituted alkylene;

b) asymmetrically N-substituting one or more of the protected amino groups of the product of step (a) with a substituent.

16. A process according to claim 15, wherein step (a) comprises reacting the symmetrical ligand with a protecting reagent comprising an optionally substituted alkylene group,

preferably the protecting reagent is an aldehyde, more preferably an aldehyde selected from formaldehyde or benzaldehyde.

17. A process for the reaction of:

(i) carbon dioxide with an epoxide;

(ii) an epoxide and an anhydride; and/or

(iii) a lactide and/or a lactone,

in the presence of a catalyst as claimed in any one of claims 1 to 11, optionally wherein the process is carried out in the presence of a chain transfer agent.