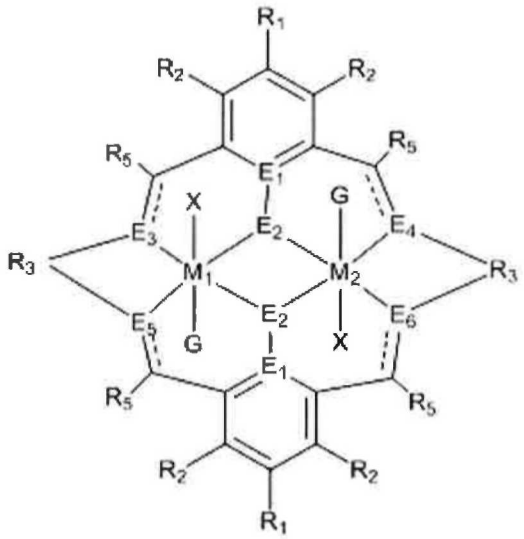
Claims

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

wherein at least one of M_1 or M_2 is selected from Ni(II) and Ni(III)-X;

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

R_3 is independently selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene, may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic; R_5 is independently selected from H, or optionally substituted

aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;

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

E3, E4, E5 and E6 are selected from N, NR_4, O and S, wherein when E3, E4, E5 or E6 are N, ------is ═══, and wherein when E3, E4, E5 or E6 are NR_4, O or S, ------is ———; R_4 is independently selected from hydrogen, 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, nitro, 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.

2. The catalyst of claim 1, wherein at least one of M_1 or M_2 is Ni(II), preferably, wherein both M_1 and M_2 are Ni(II).

3. The catalyst of any preceding claim, wherein one of M_1 or M_2 is selected from Ni(II) and Ni(III)-X and the remaining occurrence of M_1 and M_2 is selected from Zn(II), Cr(III)-X, Cr(II), Co(III)-X, Co(II), Cu(II), Mn(III)-X, Mn(II), Mg(II), Ni(II), Ni(III)-X, Fe(II), Fe(III)-X, Ti(II), Ti(III)-X, V(II), V(III)-X, Ge(IV)-$(X)_2$ and Ti(IV)-$(X)_2$, preferably, wherein the remaining occurrence of M_1 and M_2 is selected from any of: Zn(II), Mg(II), Ni(II), Co(II), Co(III)-X and Ni(III)-X.

4. The catalyst of any preceding claim, wherein R_3 is selected from substituted or unsubstituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, and cycloalkylene, preferably R_3 is selected from substituted or unsubstituted alkylene, cycloalkylene, heteroalkylene, and arylene.

5. The catalyst of any preceding claim, wherein E3, E4, E5 and E6 are NR_4.

6. The catalyst of any preceding claim, wherein R_4 is selected from hydrogen or an optionally substituted alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, aryl or heteroaryl, such as hydrogen, methyl, ethyl, benzyl, isopropyl, t-butyl, phenyl, or –CH_2-pyridine, preferably R_4 is hydrogen.

7. The catalyst of any preceding claim, wherein R_1 is selected from hydrogen, halide, amino, nitro, sulfoxide, sulfonyl, sulfinate, silyl, silyl ether, and optionally substituted alkyl, alkenyl, aryl, heteroaryl, alkoxy, aryloxy, arylthio or alkylthio, such as hydrogen, $C_{1\text{-}6}$alkyl (e.g. haloalkyl), alkoxy, aryl, halide, nitro, sulfonyl, silyl and alkylthio, for example, hydrogen, t-butyl, isopropyl, methyl, methoxy, nitro, SO_2CH_3, triethylsilyl, halogen or phenyl.

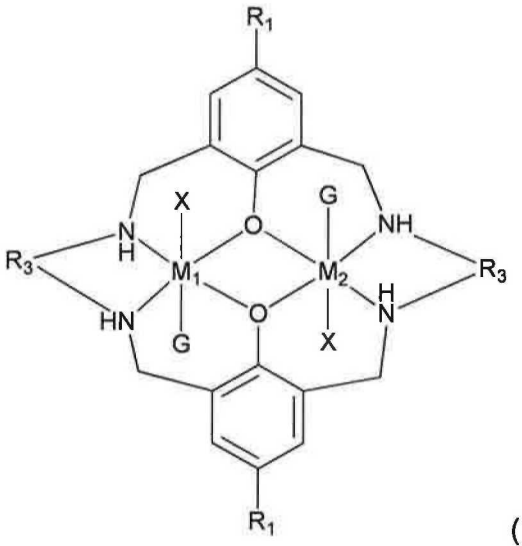
8. The catalyst of any preceding claim, wherein X is selected from $OC(O)R^x$, OSO_2R^x, $OS(O)R^x$, $OSO(R^x)_2$, $S(O)R^x$, OR^x, phosphinate, halide, nitrate, hydroxyl, carbonate, amino, nitro, amido, and optionally substituted alkyl, heteroalkyl, (for example silyl), alicyclic, heteroalicyclic, aryl or heteroaryl, preferably $OC(O)R^x$, OSO_2R^x, $OS(O)R^x$, $OSO(R^x)_2$, $S(O)R^x$, OR^x, halide, nitrate, hydroxyl, carbonate, amino, nitro, amido, alkyl (e.g. branched alkyl), heteroalkyl, (for example silyl), aryl or heteroaryl, more preferably $OC(O)R^x$, OR^x, halide, carbonate, amino, nitro, alkyl, aryl, heteroaryl, phosphinate or OSO_2R^x, preferably, wherein X is $OC(O)R^x$, wherein optionally R^x is an optionally substituted alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl, cycloalkyl or alkylaryl.

9. The catalyst of claim 1, wherein both occurrences of R_1 are the same, and are selected from hydrogen, halide, amino, nitro, sulfoxide, sulfonyl, sulfinate, silyl, silyl ether and an optionally substituted alkyl, alkenyl, aryl, heteroaryl, alkoxy, aryloxy or alkylthio; R_2 is hydrogen; both occurrences of R_3 are the same, and are selected from substituted or unsubstituted alkylene and substituted or unsubstituted arylene; E_1 is C and E_2 is O; E3, E4, E5 and E6 are NR_4; R_4 is hydrogen; each X is the same, and is selected from $OC(O)R^x$, OR^x, halide, carbonate, amino, nitro, alkyl, aryl, heteroaryl, phosphinate or OSO_2R^x, each R^x is the same and is selected from alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl or alkylaryl; each G (where present) is the same and is selected from

halide; water; a heteroaryl optionally substituted by alkyl, alkenyl, alkynyl, alkoxy, halogen, hydroxyl, nitro or nitrile; and one of M_1 and M_2 is Ni(II) or Ni(III)-X, and the remaining M_1 or M_2 is selected from Mg(II), Zn(II), Cr(III)-X, Co(II), Co(III)-X Mn(II), Ni(II), Ni(III)-X, Fe(II), and Fe(III)-X, preferably the remaining M_1 or M_2 is selected from Mg(II), Zn(II), Ni(II) and Ni(III)-X.

10. The catalyst of claim 9, wherein R_1 is hydrogen, halide, silyl, silyl ether, sulfonyl or optionally substituted alkyl or alkoxyl, preferably wherein G is absent.

11. The catalyst of claim 1, of the formula (Ib):



(Ib)

wherein:

both occurrences of R_1 are the same, and are selected from hydrogen, halide, amino, nitro, sulfoxide, sulfonyl, sulfinate, silyl, silyl ether and an optionally substituted alkyl, alkenyl, aryl, heteroaryl, alkoxy, aryloxy or alkylthio;

R_3 is selected from substituted or unsubstituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene or heteroalkynylene, cycloalkylene or arylene;

each X is the same, and is selected from $OC(O)R^x$, OR^x, halide, carbonate, amino, nitro, alkyl, aryl, heteroaryl, phosphinate or OSO_2R^x, R^x is alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl or alkylaryl;

R^x is alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl or alkylaryl;

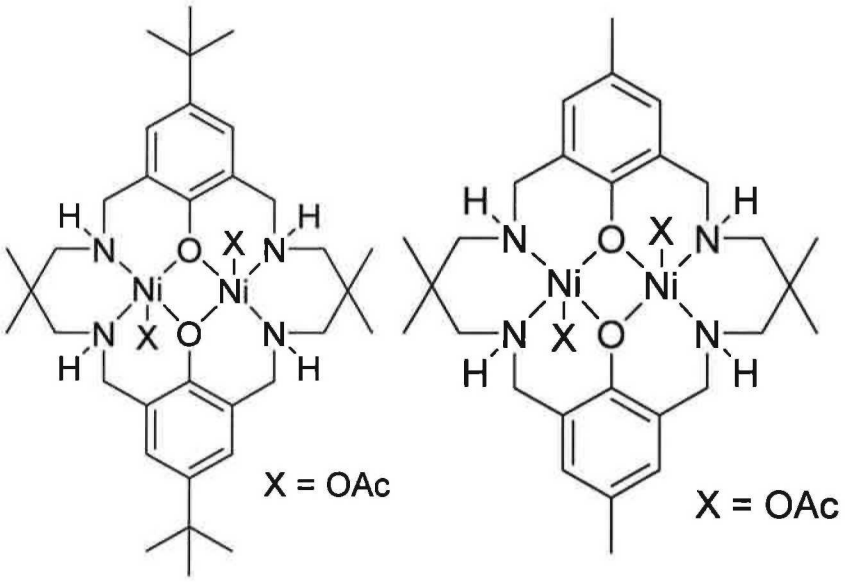
each G (where present) is independently selected from halide; water; a heteroaryl optionally substituted by alkyl, alkenyl, alkynyl, alkoxy, halogen, hydroxyl, nitro or nitrile; and

one occurrence of M_1 and M_2 is Ni(II) or Ni(III)-X, and the remaining occurrence of M_1 or M_2 is selected from Mg(II), Zn(II), Cr(III)-X, Co(II), Co(III)-X, Mn(II), Ni(II), Ni(III)-X, Fe(II), and Fe(III)-X.

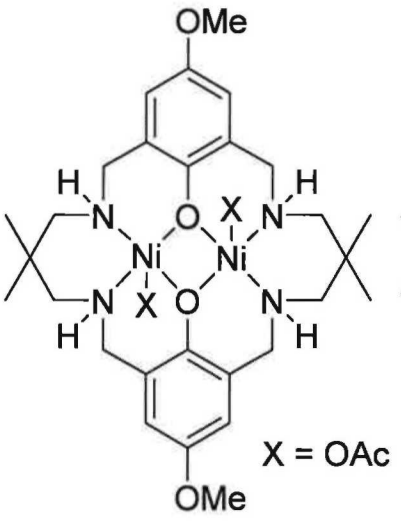
12. The catalyst of claim 9, 10 or 11, wherein M_1 and M_2 are selected from Ni(II) and Ni(III)-X, preferably both M_1 and M_2 are Ni(II).

13. The catalyst of claim 11 or 12, wherein X is $OC(O)R^x$, OR^x, halide, alkyl, aryl, heteroaryl, phosphinate or OSO_2R^x, preferably $OC(O)R^x$, and wherein R^x is optionally alkyl, alkenyl, alkynyl, heteroalkyl, aryl, heteroaryl or alkylaryl, preferably alkyl.

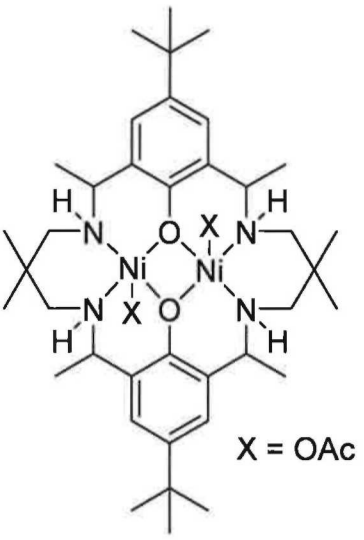
14. The catalyst of claim 1 of the formula:



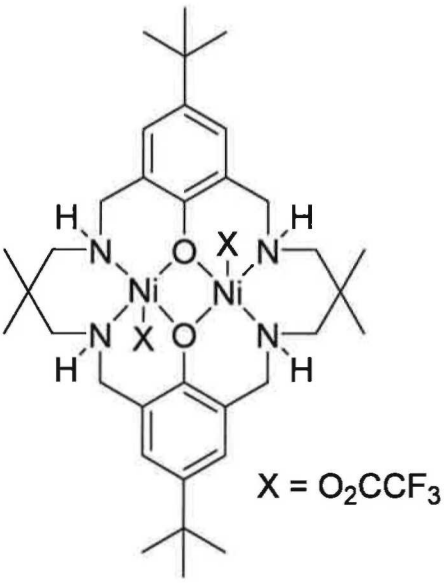
$[L^1Ni_2(OAc)_2]$ **$[L^2Ni_2(OAc)_2]$**



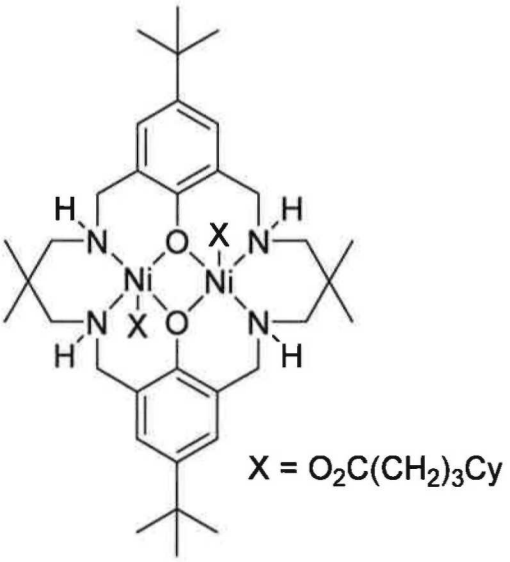
$[L^3Ni_2(OAc)_2]$



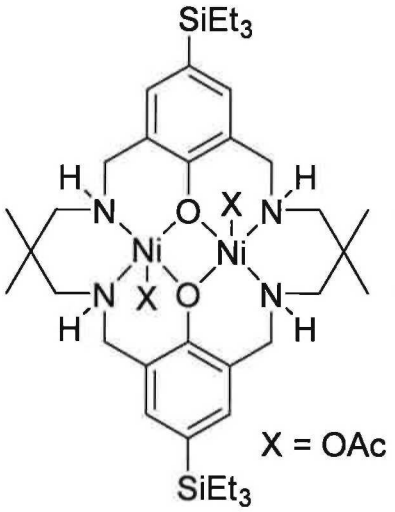
$[L^4Ni_2(OAc)_2]$

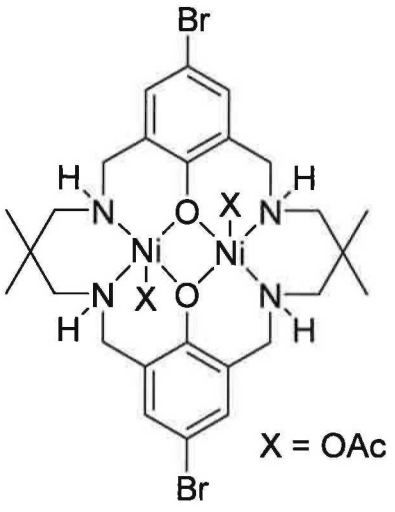


$[L^1Ni_2(O_2CCF_3)_2]$

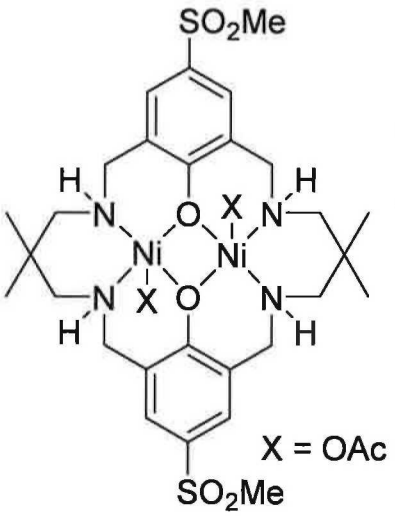


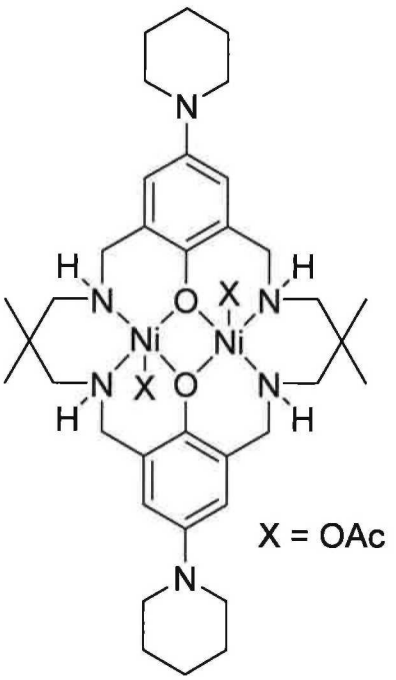
$[L^1Ni_2(O_2C(CH_2)_3Cy)_2]$



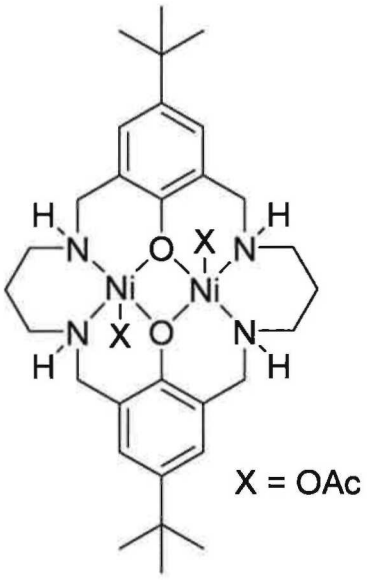


[$L^5Ni_2(OAc)_2$] **[$L^6Ni_2(OAc)_2$]**

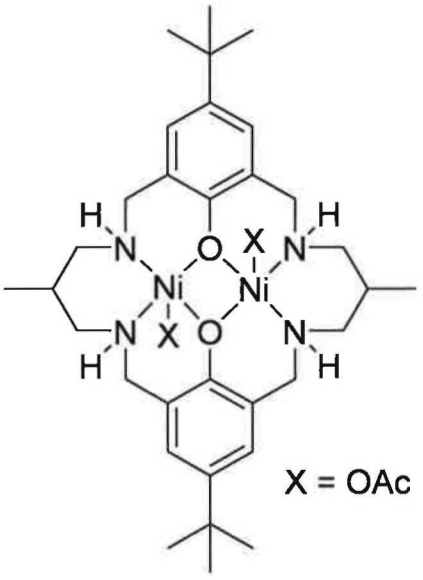




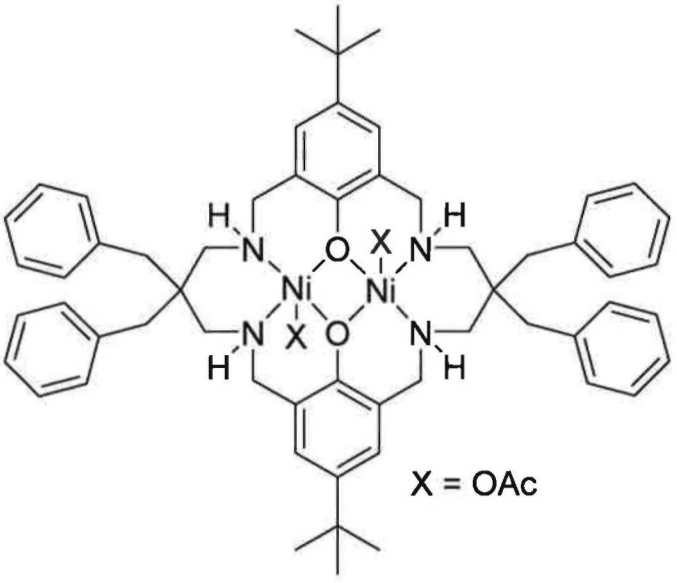
[$L^7Ni_2(OAc)_2$] **[$L^8Ni_2(OAc)_2$]**



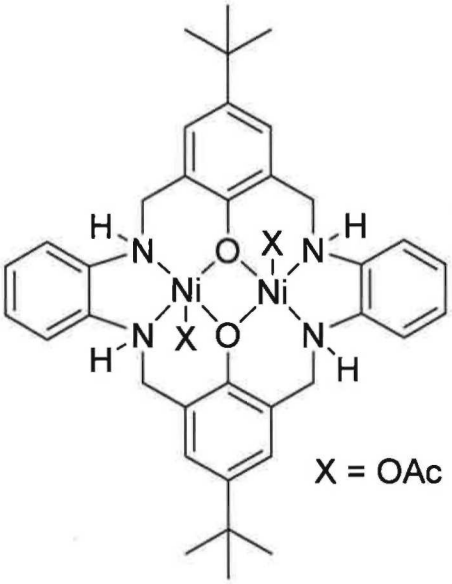
[$L^{9}Ni_2(OAc)_2$]



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

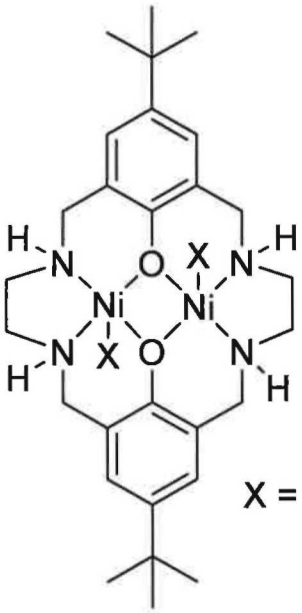


[$L^{11}Ni_2(OAc)_2$]



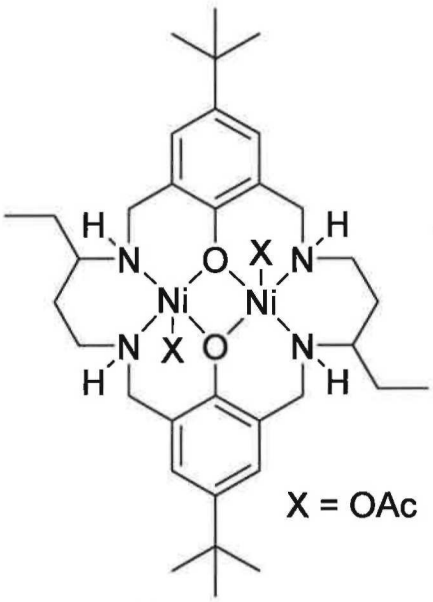
X = OAc

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



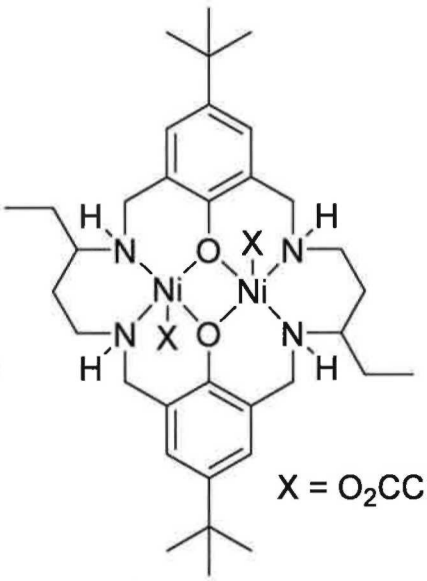
X = OAc

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



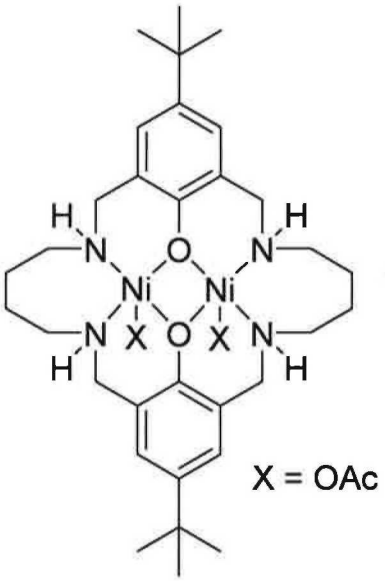
X = OAc

$[L^{14}Ni_2(OAc)_2]$

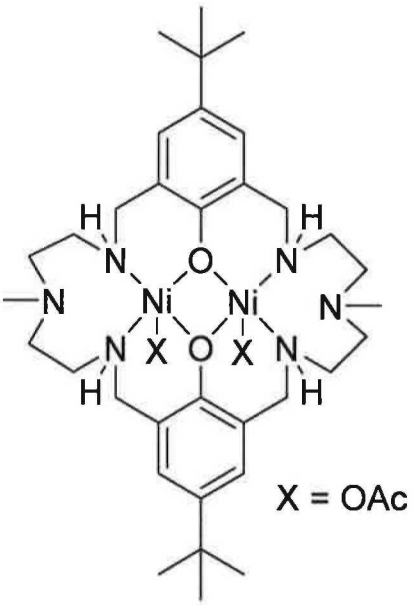


X = O_2CCF_3

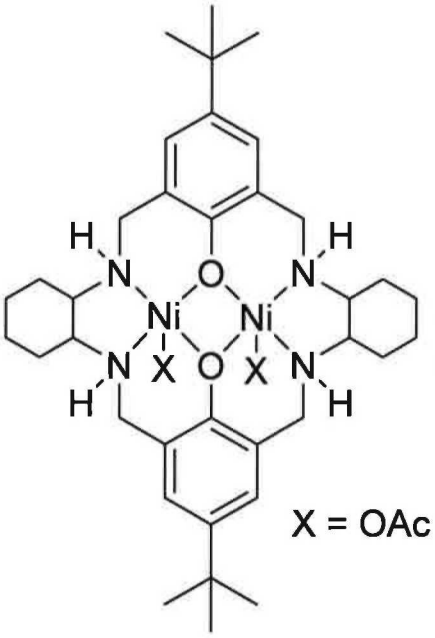
$[L^{14}Ni_2(O_2CCF_3)_2]$



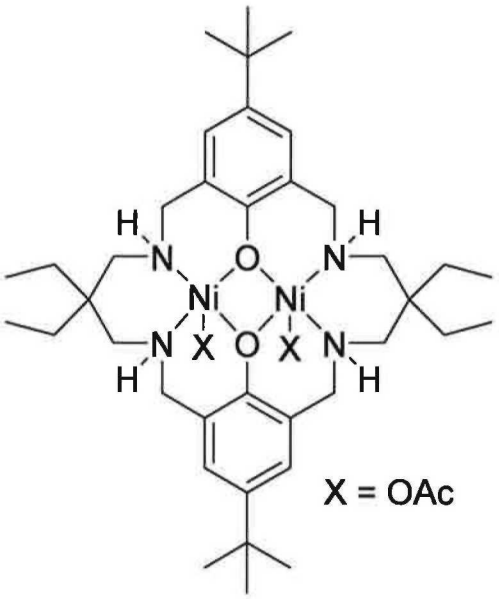
$[L^{15}Ni_2(OAc)_2]$



$[L^{16}Ni_2(OAc)_2]$



$[L^{17}Ni_2(OAc)_2]$



$[L^{18}Ni_2(OAc)_2]$

15. A process for the reaction of:

a. carbon dioxide with an epoxide;

b. an epoxide and an anhydride; and/or

c. a lactide and/or a lactone,

in the presence of a catalyst as claimed in any one of claims 1 to 14, optionally wherein the process is carried out in the presence of a chain transfer agent.