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(54) Title: DICARBONYL RUTHENIUM AND OSMIUM CATALYSTS

(57) Abstract: The disclosure relates to dicarbonyl complexes of ruthenium and osmium with bi- and tridentate nitrogen and phosphine ligands. The disclosure relates to methods for preparing these complexes and the use of these complexes, isolated or prepared in situ, as catalysts for reduction reactions of ketones and aldehydes both via transfer hydrogenation or hydrogenation with hydrogen.



“DICARBONYL RUTHENIUM AND OSMIUM CATALYSTS”**DESCRIZIONE**

The disclosure relates to dicarbonyl complexes of ruthenium and osmium with bi- and tridentate nitrogen and phosphine ligands. The disclosure relates to methods for preparing these complexes and the use of these complexes, isolated or prepared in situ, as catalysts for reduction reactions of ketones and aldehydes both via transfer hydrogenation or hydrogenation with hydrogen.

State of the art

The carbonyl compounds (aldehydes and ketones) can be easily reduced to alcohols by molecular hydrogen (hydrogenation) or donor molecules of hydrogen (transfer hydrogenation) through the use of catalysts based on rhodium, iridium, iron, ruthenium and osmium.

The development of complexes that catalyze the chemo- and stereo-selective reduction of carbonyl compounds is a subject of considerable academic and industrial interest, a target which can be achieved through the fine-tuning of the ligands of the complexes.

The hydrogenation, which entails the use of hydrogen under pressure, is an industrial process for the synthesis of alcohols. A significant breakthrough for the development and application of this process was given in the late '90s by a new class of ruthenium complexes of formula $\text{RuCl}_2(\text{P})_2(\text{diamine})$ and $\text{RuCl}_2(\text{PP})(\text{diamine})$ (P=phosphine and PP=diphosphine) for the catalytic enantioselective hydrogenation of ketones. By using a suitable combination of chiral diphosphine and diamine ligands, these complexes were proven to efficiently catalyze the asymmetric reductions of carbonyl compounds with production of chiral alcohols with high enantiomeric excess.

In addition to hydrogenation, the transfer hydrogenation reaction has also been developed using 2-propanol or formic acid as hydrogen source, with the advantage of employing non-pressure systems and reducing the risk.

In 2004 Baratta and collaborators have developed ruthenium complexes containing phosphines and bi- and tri-dentate aminopyridine ligands which show high catalytic activity in hydrogenation and transfer hydrogenation.

5 It is worth pointing out that the dicarbonyl derivative $\text{RuCl}_2(\text{CO})_2(\text{bipy})$ containing a bidentate nitrogen ligand (L. Spiccia et al., *Coord. Chem. Rev.* 2004, 248, 1329) shows catalytic activity for several processes, including the epoxidation of olefins, the water gas shift reaction and the photochemical and electrochemical reduction of CO_2 . The

cyclometallated carbonyl derivatives $[\text{RuCl}(\text{CN})(\text{CO})_2]_2$ show catalytic activities in the alkyne dimerization reaction and in the oxidation of alcohols to ketones.

The interest in these systems stems from the fact that the presence of a Ru-CO bond makes the catalyst more robust and less sensitive to the decarbonylation reactions of the substrates which can deactivate the catalysts, preventing their use in very low quantities.

Moreover, to make the reduction of carbonyl compounds to alcohols economically competitive, via transfer hydrogenation or hydrogenation, the development of catalysts with high chemo- and stereo-selectivity is a crucial issue.

Furthermore, the catalysts have to display high productivity and should be easily prepared from commercially available starting material through simple and safe synthetic routes.

The purpose of the present invention relates to the synthesis of complexes of ruthenium and osmium containing two CO ligands in combination with bidentate and tridentate nitrogen ligands and phosphorus-containing ligands. These complexes can be used as catalysts in the reduction of carbonyl compounds by transfer hydrogenation or hydrogenation with molecular hydrogen.

A further object of the present invention is to obtain ruthenium (II) and osmium (II) complexes which can be generated in situ during the reduction of carbonyl compounds or by transfer hydrogenation or hydrogenation with molecular hydrogen.

Summary of the invention

In order to achieve the purposes mentioned above, the inventors have identified in a series of dicarbonyl complexes of ruthenium and osmium, containing nitrogen and phosphine ligands, the solution for obtaining catalysts of high catalytic activity in hydrogenation reactions with molecular hydrogen and transfer hydrogenation of carbonyl compounds to alcohols.

Accordingly, the present disclosure refers to a hexacoordinate complex of formula (1):



wherein

M = Ru or Os;

X and Y are independently selected among halides, hydride, C1-C20 carboxylates and C1-C20 alkoxides;

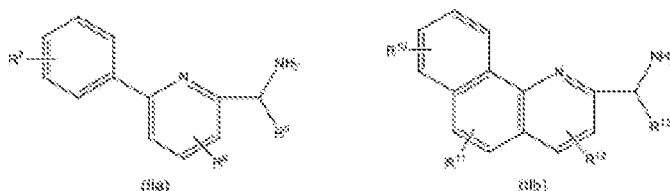
10 W is selected among halides, C1-C20 carboxylates and C1-C20 alkoxides;

- L is a nitrogen-containing ligand selected among:

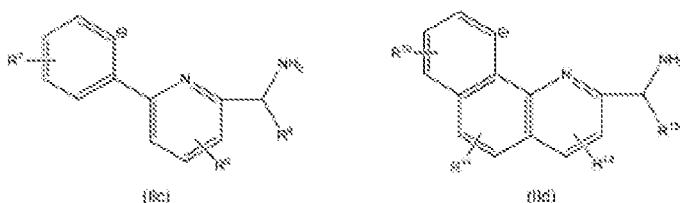
(I) a (NN) compound of formula Ia - Ic:



(II) a (HCNN) compound of formula IIa – IIb:

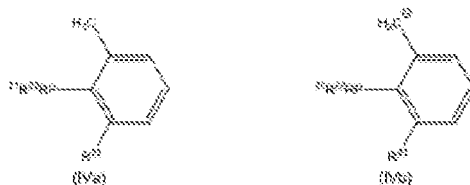


5 (III) a (CNN) ligand of formula IIc – IId:



wherein $R^1 - R^{13}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; and

10 - L' is at least one phosphorus-containing ligand selected among a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



wherein

$R^{21} - R^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups;

15 and wherein

a, b, c and e are independently 0 or 1;

d is 0,1 or 2; and

provided that when M is Ru and

- a = b = 1; c = e = 0; d = 2 and X = Y = Cl, R^{23} is not hydrogen;

- $a = 1$; $b = c = e = 0$; $d = 2$ and $X = \text{Cl}$, HCP is not (2,6-dimethylphenyl) diphenylphosphine (Hdmpp) and CP is not the anion of (2,6-dimethylphenyl) diphenylphosphine (dmpp); and

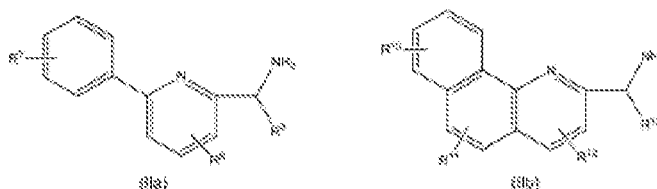
- $a = b = c = 1$; $d = e = 0$ and $X = Y = \text{Cl}$, L is not ethylenediamine or bipyridine.

5 In a further aspect, the present disclosure refers to a process to obtain the complex of formula (1) comprising:

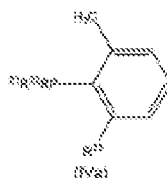
(i) reacting a compound of formula MX_2Y , wherein M, X and Y are as defined above, with HCOOH , thereby obtaining an intermediate compound of formula $[\text{MXY}(\text{CO})_2]_n$;

10 (ii) reacting the compound of formula $[\text{MXY}(\text{CO})_2]_n$ with at least one ligand selected among:

- a (HCNN) compound of formula IIa – IIb:



- a HCP compound of formula (IVa)



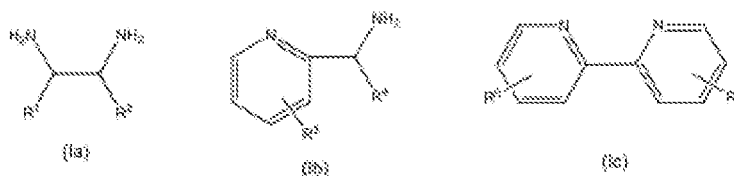
15 wherein

$\text{R}^7 - \text{R}^{13}$ and $\text{R}^{21} - \text{R}^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups

in the presence of a solvent and optionally of a tertiary amine of formula $\text{N}(\text{R}^{24}\text{R}^{25}\text{R}^{26})$, wherein R^{24} , R^{25} and R^{26} are independently selected among C1-C6 aliphatic groups;

20 and

(iii) optionally reacting the compound obtained in step (ii) with a basic compound selected among potassium carbonate, calcium carbonate and mixtures thereof and/or a nitrogen-containing (NN) compound of formula Ia-Ic:



wherein R¹ – R⁶ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups.

In a further aspect, the present disclosure refers to the use of said ruthenium or osmium complexes as catalysts or pre-catalyst for the reduction reaction of ketones or aldehydes to alcohols by transfer hydrogenation or hydrogenation with molecular hydrogen.

This and other aspects as well as the characteristics and advantages of the present invention will be more apparent from the detailed description below and by the preferred embodiments given as non-limiting illustrations of the invention itself.

Description of the invention

As used therein, “aliphatic group” refers to acyclic or cyclic, linear or branched, saturated or unsaturated hydrocarbon, excluding aromatic groups.

As used therein, “substituted aliphatic group” refers to an aliphatic group in which at least one hydrogen atom is replaced by at least one substituent group selected among –OR, –NRR', –NRCOR', –NO₂, –NH₂, –COR, –COOR, –CONRR' and halides, wherein R and R' are equal or different and can be a H or a C1-C20 aliphatic or aromatic group.

As used therein, “aromatic group” also includes substituted aromatic groups and heteroaromatic groups.

As used therein, “substituted aromatic group” refers to aromatic groups in which at least one aromatic hydrogen atom is replaced with at least one substituent group selected among –R, –OR, –NRR', –NRCOR', –NO₂, –NH₂, –COR, –COOR, –CONRR' and halides, wherein R and R' are equal or different and can be a H or a C1-C20 aliphatic or aromatic group.

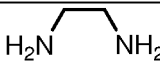
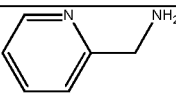
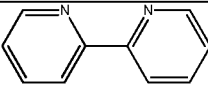
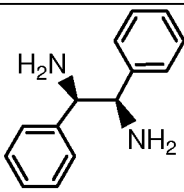
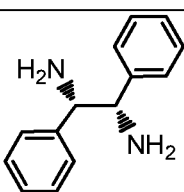
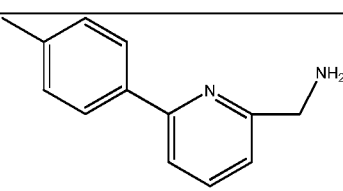
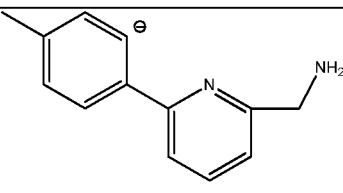
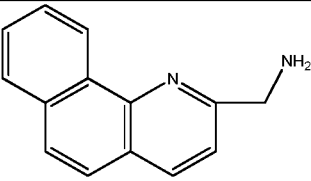
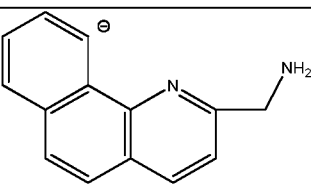
As used therein, “heteroaromatic group” refers to aromatic groups in which at least one carbon atom which is part of the aromatic ring is replaced with one heteroatom selected among N, S, O and P.

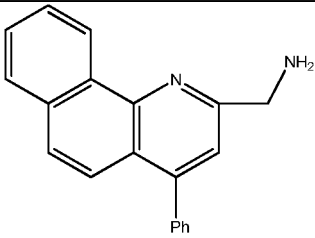
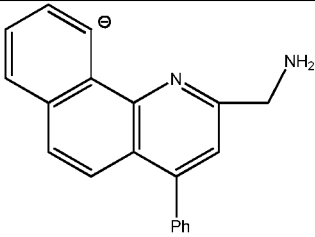
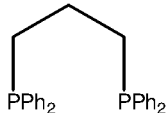
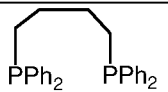
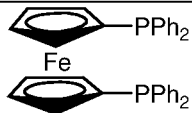
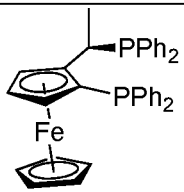
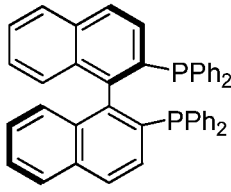
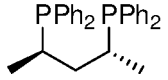
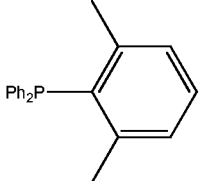
As used therein, “hydrogen-donor” refers to a compound that transfers a hydrogen atom to another compound.

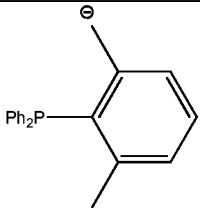
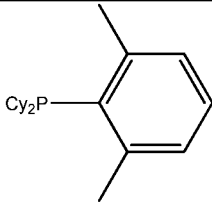
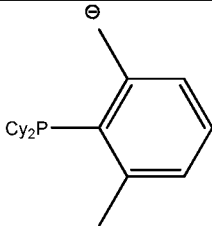
As used therein, “(transfer)hydrogenation” refers to hydrogenation with molecular hydrogen or to transfer hydrogenation using a hydrogen donor compound.

In the present description and appended claims the abbreviations listed in Table 1 are used:

Table 1. Abbreviation of the nitrogen and phosphorus ligands

Chemical name	Abbreviation	Structural formula
<i>Nitrogen-containing ligand L</i>		
ethylenediamine	en	
2-(aminomethyl)pyridine	ampy	
bipyridine	bipy	
(1 <i>R</i> ,2 <i>R</i>)-1,2-diphenylethylenediamine	(<i>R,R</i>)-dpen	
(1 <i>S</i> ,2 <i>S</i>)-1,2-diphenylethylenediamine	(<i>S,S</i>)-dpen	
6-(4-methylphenyl)-2-(aminomethyl)pyridine	Hamtp	
Anionic form of 6-(4-methylphenyl)-2-(aminomethyl)pyridine	amtp	
2-(aminomethyl)benzo[<i>h</i>]quinoline	Hambq	
Anionic form of 2-(aminomethyl)benzo[<i>h</i>]quinoline	ambq	

4-phenyl-2-(aminomethyl)benzo[<i>h</i>]quinoline	Hambq ^{Ph}	
Anionic form of 4-phenyl-2-(aminomethyl)benzo[<i>h</i>]quinoline	ambq ^{Ph}	
<i>phosphorus-containing ligand L'</i>		
triphenylphosphine	PPh ₃	
tricyclohexylphosphine	PCy ₃	
triisopropylphosphine	P <i>i</i> Pr ₃	
1,3-bis(diphenylphosphino)propane	dppp	
1,4-bis(diphenylphosphino)butane	dppb	
1,1'-bis(diphenylphosphino)ferrocene	dppf	
(R)-1-[(S _P)-2-(diphenylphosphino)ferrocenylethyl]diphenylphosphine	(R)-Josiphos	
(R)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene	(R)-BINAP	
(R,R)-Skewphos	(R,R)-BDPP	
(2,6-dimethylphenyl)diphenylphosphine	Hdmpp	

Anionic form of (2,6-dimethylphenyl)diphenylphosphine	dmpp	
(2,6-dimethylphenyl)dicyclohexylphosphine	Hdmppc	
Anionic form of (2,6-dimethylphenyl)dicyclohexylphosphine	dmppc	

The present disclosure refers to a hexacoordinate complex of formula (1):



5 wherein

M = Ru or Os;

X and Y are independently selected among halides, hydride, C1-C20 carboxylates and C1-C20 alkoxides;

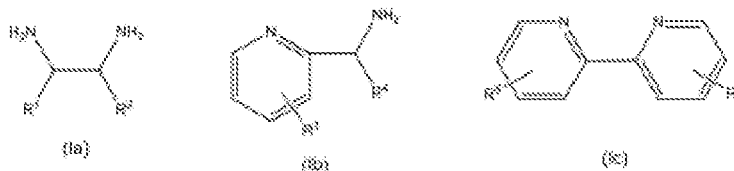
W is selected among halides, C1-C20 carboxylates and C1-C20 alkoxides;

10 a, b, c and e are independently 0 or 1;

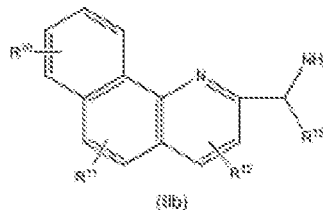
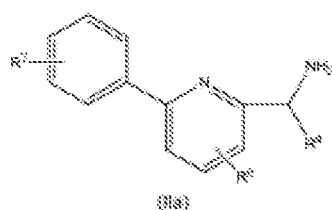
d is 0, 1 or 2;

- L is a nitrogen-containing ligand selected among:

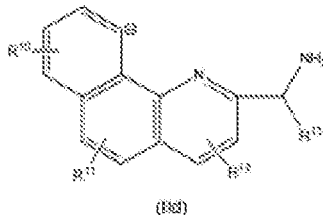
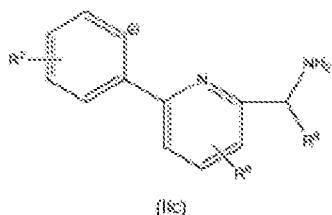
(I) a (NN) compound of formula Ia - Ic:



15 (II) a (HCNN) compound of formula IIa – IIb:

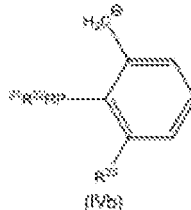
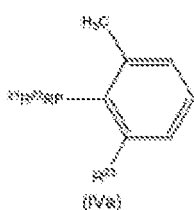


(III) a (CNN) ligand of formula IIc – IId:



wherein

- 5 $R^1 - R^{13}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R^1 and R^2 may be independently selected among H and a phenyl group and/or R^3-R^6 and R^8-R^{13} may be H and/or R^7 may be 4-methyl; and
- L' is at least one phosphorus-containing ligand selected among a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



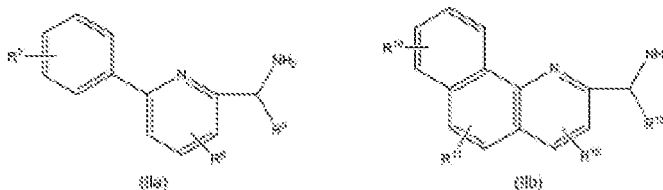
wherein

- $R^{21} - R^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be C6-C20 cycloaliphatic group or C6-C20 aromatic group, more preferably R^{23} may be $-CH_3$
- 15 and/or $R^{21} - R^{22}$ may be independently selected among phenyl and cyclohexyl group;
- provided that when M is Ru and
- $a = b = 1$; $c = e = 0$; $d = 2$ and $X = Y = Cl$, R^{23} is not hydrogen;
 - $a = 1$; $b = c = e = 0$; $d = 2$ and $X = Cl$, HCP is not (2,6-dimethylphenyl) diphenylphosphine (Hdmpp) and CP is not the anion of (2,6-dimethylphenyl) diphenylphosphine (dmpp);
 - 20 - $a = b = c = 1$; $d = e = 0$ and $X = Y = Cl$, L is not ethylenediamine or bipyridine.

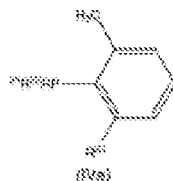
The present disclosure also refers to a process to obtain the complex of formula (1) comprising:

- (i) reacting a compound of formula MX_2Y , preferably of formula MX_3 , more preferably of formula MCl_3 , wherein M, X and Y are as defined above, with HCOOH , thereby obtaining an intermediate compound of formula $[\text{MXY}(\text{CO})_2]_n$, preferably of formula $[\text{MX}_2(\text{CO})_2]_n$, more preferably of formula $[\text{MCl}_2(\text{CO})_2]_n$;
- (ii) reacting the compound of formula $[\text{MXY}(\text{CO})_2]_n$ with at least one ligand selected among:

- a (HCNN) compound of formula IIa – IIb:



- a HCP compound of formula (IVa)



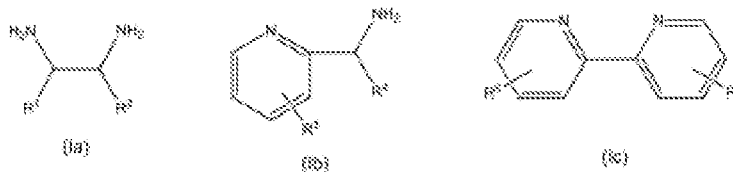
wherein

$\text{R}^7 - \text{R}^{13}$ and $\text{R}^{21} - \text{R}^{23}$ are independently selected among H, a C1-C20 aliphatic group and a C5-C20 aromatic group, preferably $\text{R}^8 - \text{R}^{13}$ may be H and/or R^7 may be 4-methyl and/or R^{23} may be $-\text{CH}_3$ and/or $\text{R}^{21} - \text{R}^{22}$ may be C6-C20 cycloaliphatic group or C6-C20 aromatic group, more preferably R^{23} may be $-\text{CH}_3$ and/or $\text{R}^{21} - \text{R}^{22}$ may be independently selected among phenyl and cyclohexyl groups,

in the presence of a solvent, preferably selected among C1-C6 aliphatic alcohols, more preferably selected among ethanol, methanol or mixtures thereof,

and optionally of a tertiary amine of formula $\text{N}(\text{R}^{24}\text{R}^{25}\text{R}^{26})$, wherein R^{24} , R^{25} and R^{26} are independently selected among C1-C6 aliphatic group, preferably triethylamine; and

- (iii) optionally reacting the compound obtained in step (ii) with a basic compound selected among potassium carbonate, calcium carbonate and mixtures thereof and/or a nitrogen-containing (NN) compound of formula Ia-Ic:



wherein $R^1 - R^6$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; preferably, R^1 and R^2 may be independently selected among H and a phenyl group and/or R^3-R^6 and R^8-R^{13} may be H and/or R^7 may be 4-methyl.

- 5 After step (iii) the complex of formula (1) may be recovered from the solution by known techniques, such as by precipitation with suitable organic solvents.

The high modularity of the nitrogen-containing ligands (Ia-c) and (IIa-d) in combination with (HCP) and (CP) allows to obtain a large number of well-defined catalysts displaying high chemo- and stereoselectivity.

For the purposes of the present invention, from the combination of the different meanings of M, X, Y, W, L, and L', the complexes of sub-formulas (V)-(IX) given below may be obtained, which are encompassed by the general formula (1).

The ligands of the type HCNN (IIa-b) have the ability to act both as bidentate (IIa-b) or tridentate ligands of the type (IIc-d). In the case of bidentate ligand the coordination occurs through the nitrogen atom of the NH_2 group and a second nitrogen atom of the heterocycle.

Thus, according to an embodiment, the present disclosure may refer to a complex of formula (V):



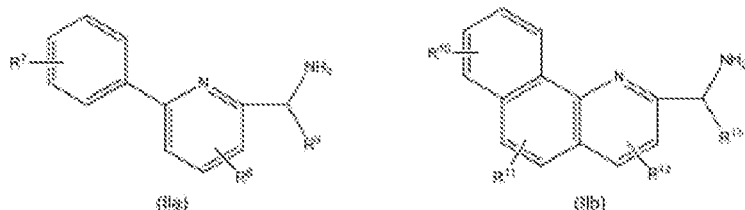
wherein M, X, Y and (HCNN) are as defined in formula (1).

- 10 The complex of formula (V) containing a HCNN ligand lead to a catalyst with a remarkably higher activity with respect to similar compounds known in the art containing a (NN) ligand.

The present disclosure also refers to a process to obtain complexes of formula (V) comprising:

- 15 (i) reacting a compound of formula MX_2Y , preferably of formula MX_3 , more preferably of formula MCl_3 , wherein M, X and Y are as defined above, with $HCOOH$, thereby obtaining an intermediate compound of formula $[MXY(CO)_2]_n$, preferably of formula $[MX_2(CO)_2]_n$, more preferably of formula $[MCl_2(CO)_2]_n$;

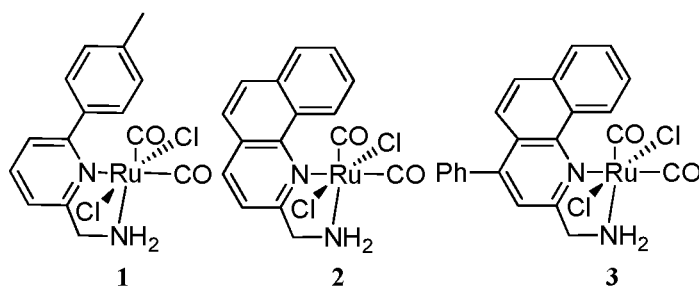
(ii) reacting the compound of formula $[MX(Y)(CO)_2]_n$ with a (HCNN) compound of formula IIa – IIb:



wherein

- 5 $R^7 - R^{13}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R^7 may be 4-methyl and/or $R^8 - R^{13}$ may be H, in the presence of solvent, preferably selected among a C1-C6 aliphatic alcohol, more preferably selected among ethanol, methanol and mixtures thereof.

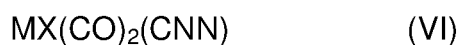
Non limiting examples of preferred complexes of formula (V) are:



- 10 The neutral dicarbonyl complexes **1-3** were obtained by treatment of $[RuCl_2(CO)_2]_n$ polymer (prepared from $RuCl_3 \cdot xH_2O$), with the ligands 6-(4-methylphenyl)-2-(aminomethyl)pyridine, 2-(aminomethyl)benzo[h]quinoline and 4-phenyl-2-(aminomethyl)benzo[h]quinoline, respectively, in ethanol.

The HCNN ligands of the type (IIa), which contain a pyridine ring functionalized in the 6 position with an aromatic group, and those of the type (IIb), containing the benzo[h]quinoline system, have the ability to act as anionic tridentate ligands (IIc-IId) through the nitrogen atom of the $-NH_2$ group, a second nitrogen atom of the heterocycle and a cyclometallated carbon atom with the metal.

Thus, according to a further embodiment, the present disclosure may refer to complexes of formula (VI)

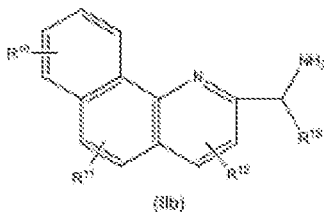
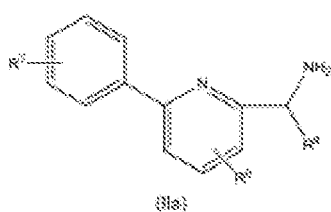


wherein M, X and (CNN) are as defined in formula (1).

- 15 The present disclosure also refers to a process to obtain complexes of formula (VI) by:
- (i) reacting a compound of formula MX_2Y , preferably of formula MX_3 , more preferably of formula MCl_3 , wherein M, X and Y are as defined above, with $HCOOH$, thereby

obtaining an intermediate compound of formula $[MXY(CO)_2]_n$, preferably of formula $[MX_2(CO)_2]_n$, more preferably of formula $[MCl_2(CO)_2]_n$;

(ii) reacting the compound of formula $[MXY(CO)_2]_n$ with a (HCNN) compound of formula IIa – IIb:



5

wherein

$R^7 - R^{13}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R^7 may be 4-methyl and/or $R^8 - R^{13}$ may be H,

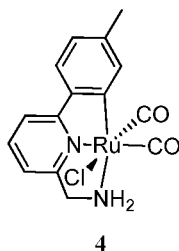
in the presence of a solvent, preferably selected among C1-C6 aliphatic alcohols, more preferably selected among ethanol, methanol and mixtures thereof

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and of a tertiary amine of formula $N(R^{24}R^{25}R^{26})$, wherein R^{24} , R^{25} and R^{26} are s independently selected among C1-C6 aliphatic group, preferably triethylamine; and

(iii) reacting the compound obtained in step (ii) with a basic compound selected among potassium carbonate, calcium carbonate and mixtures thereof.

Non limiting example of preferred complexes of formula (VI) is:



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The pincer dicarbonyl complex **4** was synthesized from $[RuCl_2(CO)_2]_n$ and 6-(4-methylphenyl)-2-(aminomethyl)pyridine in refluxing ethanol with triethylamine.

According to a further embodiment, the present disclosure may refer to complexes of formula (VII)

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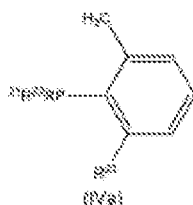
wherein M, (CP), (NN) and W are as defined in formula (1).

Preferably, R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be a C6-C20 cycloaliphatic group or C6-C20 aromatic group, more preferably R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be independently selected among phenyl and cyclohexyl group.

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The present disclosure also refers to a process to obtain complexes of formula (VII) by:

- (i) reacting a compound of formula MX_2Y , preferably of formula MX_3 , more preferably of formula MCl_3 , wherein M, X and Y are as defined above, with HCOOH , thereby obtaining an intermediate compound of formula $[\text{MXY}(\text{CO})_2]_n$, preferably of formula $[\text{MX}_2(\text{CO})_2]_n$, more preferably of formula $[\text{MCl}_2(\text{CO})_2]_n$;
- (ii) reacting the compound of formula $[\text{MXY}(\text{CO})_2]_n$ with a (HCP) compound of formula (IVa)



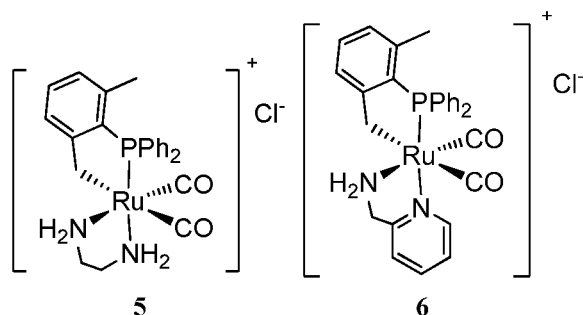
wherein

- $\text{R}^{21} - \text{R}^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R^{23} may be $-\text{CH}_3$ and/or $\text{R}^{21} - \text{R}^{22}$ may be a C6-C20 cycloaliphatic group or C6-C20 aromatic group, more preferably R^{23} may be $-\text{CH}_3$ and/or $\text{R}^{21} - \text{R}^{22}$ may be independently selected among phenyl and cyclohexyl group in the presence of a solvent, preferably selected among C1-C6 aliphatic alcohols, preferably selected among ethanol, methanol and mixtures thereof and of a tertiary amine of formula $\text{N}(\text{R}^{24}\text{R}^{25}\text{R}^{26})$, wherein R^{24} , R^{25} and R^{26} are independently selected among C1-C6 aliphatic group, preferably triethylamine; and
- (iii) reacting the compound obtained in step (ii) with a basic compound selected among potassium carbonate, calcium carbonate and mixtures thereof and a nitrogen-containing (NN) compound of formula Ia-Ic:



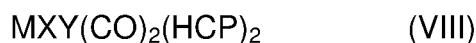
wherein $\text{R}^1 - \text{R}^6$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably $\text{R}^1 - \text{R}^2$ may be independently selected among H and phenyl group and/or $\text{R}^3 - \text{R}^6$ may be H.

Non limiting examples of preferred complexes of formula (VII) are:



The cationic dicarbonyl cyclometallated complexes **5**, **6** were prepared from $[\text{RuCl}_2(\text{CO})_2]_n$ with (2,6-dimethylphenyl)diphenylphosphine in the presence of triethylamine and the bidentate nitrogen ligand ethylenediamine or 2-(aminomethyl)pyridine in ethanol.

According to a further embodiment, the present disclosure may refer to complexes comprising the ligand (IVa) to coordinate the metal, affording complexes of formula (VIII):



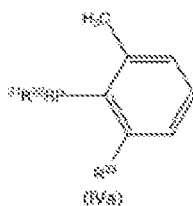
wherein M, X, Y and HCP are as defined in formula (1), provided that when M is Ru and $\text{X} = \text{Y} = \text{Cl}$, R^{23} is not hydrogen.

Preferably, R^{23} may be $-\text{CH}_3$ and/or $\text{R}^{21} - \text{R}^{22}$ may be C6-C20 cycloaliphatic groups or C6-C20 aromatic group, more preferably R^{23} may be $-\text{CH}_3$ and/or $\text{R}^{21} - \text{R}^{22}$ may be independently selected among phenyl and cyclohexyl group. The ortho-methyl group can be easily deprotonated, leading to the anionic bidentate ligand of the type (IVb) through the P and C atoms.

The present disclosure may also refer to a process to obtain complexes of formula (VIII) by:

(i) reacting a compound of formula MX_2Y , preferably of formula MX_3 , more preferably of formula MCl_3 , wherein M, X and Y are as defined above, with HCOOH , thereby obtaining an intermediate compound of formula $[\text{MXY}(\text{CO})_2]_n$, preferably of formula $[\text{MX}_2(\text{CO})_2]_n$, more preferably of formula $[\text{MCl}_2(\text{CO})_2]_n$;

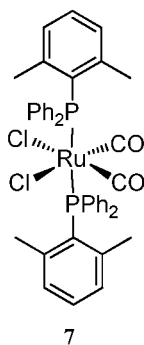
(ii) reacting the compound of formula $[\text{MXY}(\text{CO})_2]_n$ with at least one (HCP) compound of formula (IVa)



wherein

$R^{21} - R^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be a C6-C20 cycloaliphatic group or a C6-C20 aromatic group, more preferably R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be independently selected among phenyl and cyclohexyl group, in the presence of a solvent, preferably selected among C1-C6 aliphatic alcohols, more preferably among ethanol, methanol and mixtures thereof.

Non limiting examples of preferred complexes of formula (VIII) is:



The dicarbonyl complex **7** was obtained by reaction of the polymer $[RuCl_2(CO)_2]_n$ with (2,6-dimethylphenyl)diphenylphosphine, in ethanol.

According to a further embodiment, the present disclosure may refer to a complex of formula (IX)



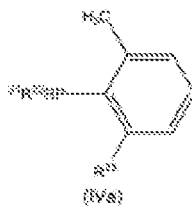
wherein M, X, CP and HCP are as defined in formula (1), provided that when M is Ru and X is Cl, HCP is not 2,6-dimethylphenyl)diphenylphosphine (Hdmpp) and CP is not the anion of 2,6-dimethylphenyl)diphenylphosphine (dmpp).

Preferably, R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be a C6-C20 cycloaliphatic group or a C6-C20 aromatic group, more preferably R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be independently selected among phenyl group and cyclohexyl group.

The present disclosure may also refer to a process to obtain complexes of formula (IX) by:

(i) reacting a compound of formula MX_2Y , preferably of formula MX_3 , more preferably of formula MCl_3 , wherein M, X and Y are as defined above, with $HCOOH$, thereby obtaining an intermediate compound of formula $[MXY(CO)_2]_n$, preferably of formula $[MX_2(CO)_2]_n$, more preferably of formula $[MCl_2(CO)_2]_n$;

(ii) reacting the compound of formula $[MXY(CO)_2]_n$ with at least one (HCP) compound of formula (IVa)



wherein

$R^{21} - R^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be a C6-C20 cycloaliphatic group or a C6-C20 aromatic group, more preferably R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be independently selected among phenyl and cyclohexyl group, in the presence of a solvent, preferably selected among C1-C6 aliphatic alcohols, more preferably among ethanol, methanol and mixtures thereof,

and of a tertiary amine of formula $N(R^{24}R^{25}R^{26})$, wherein R^{24} , R^{25} and R^{26} are independently selected among C1-C6 aliphatic group, preferably trimethylamine, thereby obtaining a pentacoordinate complex;

(iii) reacting the pentacoordinate complex with carbon monoxide in the presence of an organic solvent, preferably CH_2Cl_2 .

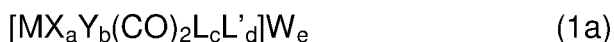
The complex of formula (1) and of sub-formulas (V)-(IX) have been found to be highly active in transfer hydrogenation of ketones and aldehydes to alcohols and can be used in hydrogenation of the same compounds using molecular hydrogen.

A further aspect of the present disclosure is therefore the use of the complex of formula (1) or of sub-formulas (V)-(IX) as catalysts or pre-catalyst for the reduction reaction of ketones or aldehydes to alcohols by transfer hydrogenation or hydrogenation with molecular hydrogen.

In another aspect, the present disclosure refers to a process for the reduction of ketones or aldehydes to the corresponding alcohols comprising the following steps:

- (a) mixing a catalyst or pre-catalyst with a solution comprising at least one base and at least one substrate selected among C3-C42 ketones and C2-C41 aldehydes thereby obtaining a mixture; and
- (b) contacting said mixture with molecular hydrogen or with at least one hydrogen-donor, preferably selected among 2-propanol, sodium formate, ammonium formate, and a mixture of formic acid and triethylamine,

said process being characterized in that the catalyst or pre-catalyst is a hexacoordinate complex of formula (1a):



wherein

M = Ru or Os;

- 5 X and Y are independently selected among halides, hydride, C1-C20 carboxylates and C1-C20 alkoxides;

W is selected among halides, C1-C20 carboxylates and C1-C20 alkoxides;

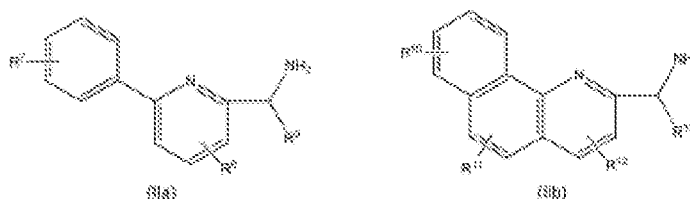
a, b, c and e are independently 0 or 1, d is 0, 1 or 2;

- L is a nitrogen-containing ligand selected among:

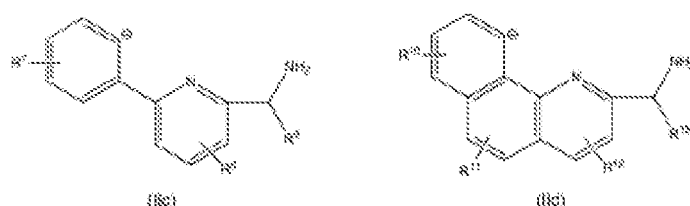
- 10 (I) a (NN) compound of formula Ia - Ic:



- (II) a (HCNN) compound of formula IIa – IIb:



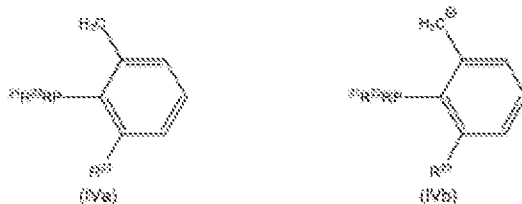
- (III) a (CNN) ligand of formula IIc – IId:



wherein

R¹ - R¹³ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R¹ and R² may be independently selected among H and a phenyl group and/or R³-R⁶ and R⁸-R¹³ may be H and/or R⁷ may be 4-methyl; and

- 20 - L' is at least one phosphorus-containing ligand selected among a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



wherein

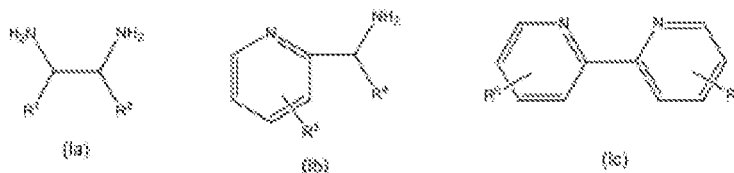
$R^{21} - R^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be a C6-C20 cycloaliphatic group or a C6-C20 aromatic group, more preferably R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be independently selected among phenyl and cyclohexyl group; provided that

when M is Ru and $a = 1$; $b = c = e = 0$; $d = 2$ and $X = Cl$, HCP is not 2,6-dimethylphenyl)diphenylphosphine (Hdmpp) and CP is not the anion of 2,6-dimethylphenyl)diphenylphosphine (dmpp).

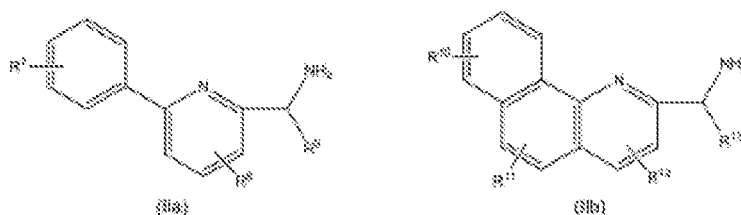
The complex of formula (1) and sub-formulas (VIII) and (IX) containing only phosphorus-containing ligands L' may be conveniently used as pre-catalyst in a (transfer)hydrogenation process carried out in the presence of a nitrogen-containing ligand L.

Therefore, according to an embodiment, the present disclosure may refer to a process for the reduction of ketones or aldehydes to the corresponding alcohols, comprising:

- (a) mixing a pre-catalyst complex of formula (2) with a solution comprising
 - at least one base and at least one substrate selected among C3-C42 ketones and C2-C41 aldehydes; and
 - at least one nitrogen-containing compound L selected among:
 - (I) a NN compound of formula Ia to Ic:



- (II) a HCNN compound of formula IIa – IIb:



wherein

$R^1 - R^{13}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R^1 and R^2 may be independently selected among H and a phenyl group and/or $R^3 - R^6$ and $R^8 - R^{13}$ may be H and/or R^7 may be 4-methyl,

thereby obtaining a mixture and

(b) contacting said mixture with molecular hydrogen or with at least one hydrogen-donor, preferably selected among 2-propanol, sodium formate, ammonium formate and a mixture of formic acid and triethylamine,

wherein said pre-catalyst has formula (2):



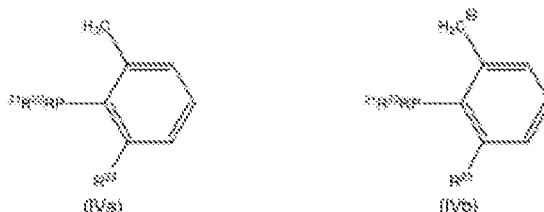
wherein

M = Ru or Os;

X and Y are independently selected among halides, hydride, C1-C20 carboxylates and C1-C20 alkoxides;

a and b are independently 0 or 1, d is 1 or 2;

- L' is at least one phosphorus-containing ligand selected among a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



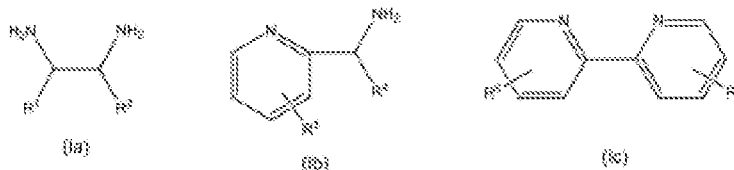
wherein

$R^{21} - R^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be a C6-C20 cycloaliphatic group or a C6-C20 aromatic group, more preferably R^{23} may be $-CH_3$ and/or $R^{21} - R^{22}$ may be independently selected among phenyl and cyclohexyl group;

provided that

when M is Ru and $a = 1$; $b = 0$; $d = 2$ and $X = Cl$, HCP is not 2,6-dimethylphenyl)diphenylphosphine (Hdmpp) and CP is not the anion of 2,6-dimethylphenyl)diphenylphosphine (dmpp).

Preferably, the nitrogen-containing compound may be selected among NN compounds of formula (Ia) to (Ic)



wherein R¹ – R⁶ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups. More preferably, the nitrogen-containing compound may be selected among ethylenediamine and 2-(aminomethyl)pyridine.

- 5 In a further embodiment, the present disclosure may refer to a process for the reduction of ketones or aldehydes to the corresponding alcohols as described above, wherein the catalyst or pre-catalyst is a complex of formula (1a) or (2) provided that when M is Ru and a = b = 1, c = e = 0, d = 2 and X = Y = Cl, R²³ is not hydrogen.

- 10 In a further embodiment, the present disclosure may refer to a process for the reduction of ketones or aldehydes to the corresponding alcohols as described above, wherein the catalyst or pre-catalyst is a complex of formula (1a), provided that when M is Ru and a = b = c = 1; d = e = 0 and X = Y = Cl, L is not ethylenediamine, 2-(aminomethyl)pyridine or bipyridine, preferably L is not a (NN) ligand.

- 15 The complex of formula (1), (V) and (VI) containing only nitrogen-containing ligands L may be conveniently used as pre-catalyst in a (transfer)hydrogenation process carried out in the presence of a phosphorus-containing ligand L'.

Therefore, according to an embodiment, the present disclosure refers to a process for the reduction of ketones or aldehydes to the corresponding alcohols, comprising:

- (a) mixing a pre-catalyst complex of formula (3) with a solution comprising
- 20 - at least one base and at least one substrate selected from the group consisting of C3-C42 ketones and C2-C41 aldehydes
- at least one phosphorus-containing compound selected among:
- (i) a phosphine (P) selected among:
- a phosphine of formula PR¹⁶R¹⁷R¹⁸, wherein R¹⁶ - R¹⁸ are independently selected
- 25 among H, C1-C20 aliphatic groups and C5-C20 aromatic groups;
- an optically active phosphine selected among (S)-neomenthyldiphenylphosphine and (R)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl;
- (i) a diphosphine (PP) selected among:
- a diphosphine of formula P(R¹⁹)₂ - Z - P(R²⁰)₂, wherein Z is a C2-C4 hydrocarbon
- 30 chain or ferrocene optionally substituted with C1-C20 aliphatic groups, and

wherein R^{19} and R^{20} are independently selected among C1-C20 aliphatic groups and C5-C20 aromatic groups;

- an optically active diphosphine selected from the group consisting of (R)-(6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine), (R)-(1,1'-binaphthalene-2,2'-diyl)bis(diphenylphosphine), (R)-(1,1'-binaphthalene-2,2'-diyl)bis[bis(3,5-dimethylmethyl)phosphine], (R)-1-{2-[diphenylphosphine]ferrocenyl}ethyldicyclohexyl phosphine, (R)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethyldicyclohexyl phosphine and (2R,4R)-2,4-bis(diphenylphosphine)pentane,

thereby obtaining a mixture; and

(b) contacting said mixture with molecular hydrogen or with at least one hydrogen-donor, preferably selected among 2-propanol, sodium formate, ammonium formate and a mixture of formic acid and triethylamine,

wherein said pre-catalyst has formula (3)



wherein

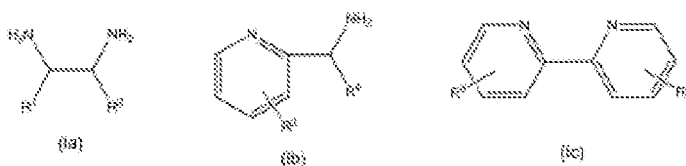
M = Ru or Os;

X and Y are independently selected among halides, hydride, C1-C20 carboxylates and C1-C20 alkoxides;

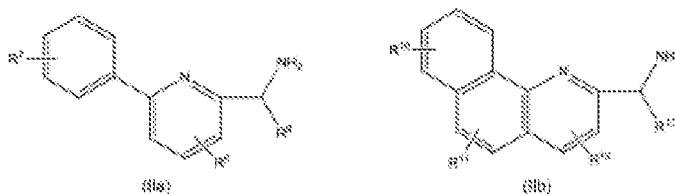
b is 0 or 1

- L is a nitrogen-containing ligand selected among:

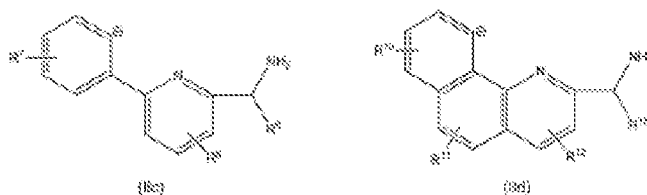
(I) a (NN) compound of formula Ia - Ic:



(II) a (HCNN) compound of formula IIa – IIb:



(III) a (CNN) ligand of formula IIc-IId:



wherein R¹ - R¹³ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups preferably R¹ and R² may be independently selected among H and a phenyl group and/or R³-R⁶ and R⁸-R¹³ may be H and/or R⁷ may be 4-methyl.

- 5 In a further embodiment, the present disclosure may refer to a process for the reduction of ketones or aldehydes to the corresponding alcohols as described above, wherein the pre-catalyst is a complex of formula (3), with the further proviso that when M is Ru, b = 1 and X = Y = Cl, L is not ethylenediamine, 2-(aminomethyl)pyridine or bipyridine, preferably L is not a (NN) ligand.

In a further embodiment, the present disclosure may refer to complexes of formula (1), (1a), (2), (3) and of sub-formulas (V)-(IX) as described above in which M is Ru.

- 10 In a further embodiment, the present disclosure may refer to a complex of formula (1), (1a), (2), (3) and sub-formulas (V), (VI), (VIII) and (IX) as described above, wherein X and/or Y is chlorine, preferably X and Y are chlorine.

In a further embodiment, the present disclosure may refer to a complex of formula (1) and (1a) and sub-formula (VII) as described above, wherein W is chlorine.

- 15 The complex of formula (1) and sub-formula (VII) containing both nitrogen- and phosphorus-containing ligands may be conveniently used as catalyst in transfer hydrogenation or hydrogenation with molecular hydrogen.

In the catalytic reduction processes described above, the step (a) of the reduction reaction is conducted in the presence of a base, wherein said base may be an alkali metal alkoxide preferably selected among sodium iso-propoxide, potassium tert-butoxide, potassium hydroxide, potassium carbonate, more preferably is potassium tert-butoxide.

- 20 In a preferred embodiment, the present disclosure may refer to a process for the reduction of ketones or aldehydes to the corresponding alcohols, wherein step (b) is carried out by contacting said mixture with molecular hydrogen.

According to a further embodiment, in the process of the disclosure in step (a) the base is sodium iso-propoxide and in step (b) the mixture is contacted with at least one hydrogen donor.

The transfer hydrogenation reduction process of the present disclosure may be carried out at a temperature of 30 - 82 °C.

In one embodiment, the reduction reactions by hydrogenation with H₂ may be carried out at 40-70 °C under hydrogen atmosphere (5–30 atm) in presence of methanol or ethanol as solvent. Under these reaction conditions the conversion of the ketone or aldehyde to alcohol is in the range from good to complete.

The complex of the present disclosure may be used for the preparation of alcohols, also chiral, by the reduction of C3-C41 ketones and of C2-C41 aldehydes.

In the process of the disclosure, at least one substrate may be selected among:

- at least one C3-C41 ketone selected among compounds of formula $R^{27}C(=O)R^{28}$ wherein R^{27} and R^{28} are independently selected among C1-C20 aliphatic, substituted aliphatic and aromatic groups, wherein optionally R^{27} and R^{28} are linked to form a cycle;
- at least one C2-C41 aldehyde is selected among compounds of formula $R^{29}C(=O)H$, wherein R^{29} is selected among C1-C40 aliphatic, substituted aliphatic and aromatic groups; and
- mixtures thereof.

According to an embodiment, in the process of the present disclosure the molar ratio substrate/catalyst or pre-catalyst may range from 1000/1 to 100000/1, preferably from 1000/1 to 50000/1.

- According to an embodiment, in the process of the present disclosure the molar ratio ligand/catalyst or pre-catalyst may range from 1/1 to 5/1, preferably from 1/1 to 2/1.

According to a further embodiment, in the process of the present disclosure the molar ratio substrate/base may range from 20 to 50.

These and other objects as well as features and advantages of the present invention will be better understood from the following detailed description and from the preferred embodiments which are given for illustrative purposes and not limitative of the invention itself.

All the syntheses of the complexes and transfer hydrogenation reactions were carried out under inert gas atmosphere and the solvents used were dried and distilled before use. All the procedures of hydrogenation were carried using technical grade solvents.

Example 1: Synthesis of the complex $RuCl_2(CO)_2(Hamtp)$ (1)

- The complex $RuCl_3 \cdot xH_2O$ (83.2 mg, 0.40 mmol, 1 equiv) was added to 6 mL of HCOOH and the suspension was stirred in a sealed tube at 110 °C for 2 h (until the mixture turned yellow and homogenous), obtaining $[RuCl_2(CO)_2]_n$. The solvent was evaporated under reduced pressure and the residue was dissolved in 6 mL of distilled

EtOH. After addition of the ligand Hamtp (78.1 mg, 0.39 mmol, 1 equiv) the solution was stirred at 80 °C overnight. The solution was evaporated under reduced pressure and the residue was dissolved in 2 mL of CHCl_3 . The solution was stirred for 1 h at room temperature and the complex was precipitated by addition of 10 mL ethyl ether. After filtration the solid was washed 2 times with 5 mL of ethyl ether, one time with 5 mL of *n*-pentane and dried under reduced pressure. Yield: 105.3 mg (80%). Anal. Calcd (%) for $\text{C}_{15}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_2\text{Ru}$: C, 42.27; H, 3.31; N, 6.57, Found: C, 42.10; H, 3.26; N, 6.59. ^1H NMR (200 MHz, CDCl_3) δ 7.80-7.30 (m, 7H, aromatic hydrogens), 4.77 (br, 2H, NH_2), 4.19 (br, 2H, NCH_2), 2.43 (s, 3H, CH_3); ^{13}C NMR (50 MHz, CDCl_3) δ 195.5, 190.3, 164.8-120.2 (m, aromatic carbons), 51.2, 21.5. IR (cm^{-1}): 2067, 1998.

Example 2: Synthesis of the complex $\text{RuCl}_2(\text{CO})_2(\text{Hambq})$ (2)

The complex $[\text{RuCl}_2(\text{CO})_2]_n$ (203 mg, 0.89 mmol, 1 equiv) suspended in ethanol (10 mL), was reacted with the ligand Hambq (202 mg, 0.97 mmol, 1.1 equiv). The suspension was stirred at 80°C overnight and the solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (4 mL) and the solution was stirred at room temperature for 4h. The volume was reduced to about 1 mL. The complex was precipitated by addition of 10 mL of ethyl ether. The obtained solid was filtered, washed two times with 5 mL of ethyl ether, one time with 5 mL of *n*-pentane and dried under reduced pressure. Yield: 190 mg (49%). Anal. Calcd (%) for $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_2\text{Ru}$: C, 44.05; H, 2.77; N, 6.42; found: C, 44.10; H, 2.78; N, 6.38. ^1H NMR (200 MHz, CD_2Cl_2) δ 8.25 (d, $J = 8.3$ Hz, 1H), 8.11 – 7.41 (m, 7H), 4.97 – 4.79 (m, 1H), 4.77 – 4.60 (m, 1H), 4.59 – 4.45 (m, 1H), 3.82 – 3.56 (m, 1H).; ^{13}C NMR (50 MHz, CD_2Cl_2) δ 199.9, 190.3, 159.9, 150.5, 141.7, 137.4, 136.7, 134.1, 129.6, 129.3, 127.7, 125.1, 122.3, 121.7, 117.2, 65.5.

Example 3: Synthesis of the complex $\text{RuCl}_2(\text{CO})_2(\text{Hambq}^{\text{Ph}})$ (3)

The complex $[\text{RuCl}_2(\text{CO})_2]_n$ (227 mg, 1.00 mmol, 1 equiv) suspended in ethanol (10 mL), was reacted with the ligand Hambq (332 mg, 1.17 mmol, 1.2 equiv). The suspension, was stirred at 80 °C overnight and the solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (4 mL) and the solution was stirred at room temperature for 4h. The volume was reduced to about 1 mL. The complex was precipitated by addition of 10 mL of ethyl ether. The obtained solid was filtered, washed two times with 5 mL of ethyl ether, once with 5 mL of *n*-pentane and dried under reduced pressure. Yield: 370 mg (72%). Anal. Calcd (%) for $\text{C}_{22}\text{H}_{16}\text{Cl}_2\text{N}_2\text{O}_2\text{Ru}$: C, 51.57; H, 3.15; N, 5.47, found: C, 51.45; H, 3.32; N, 5.71. ^1H NMR (200 MHz, CD_3OD) δ 9.60 – 9.41 (m, 1H), 8.06 – 7.40 (m, 11H), 4.62 (s, 2H). ^{13}C NMR

(50 MHz, CD₂Cl₂) δ 201.2, 194.5, 161.7, 158.4, 157.2, 150.5, 142.6, 137.8, 137.4, 134.6, 130.1, 129.9, 129.7, 129.4, 129.2, 124.0, 122.0, 121.3, 118.1, 46.1.

Example 4: Synthesis of the complex RuCl(amp)(CO)₂ (4)

The compound RuCl₃·xH₂O (107.3 mg, 0.51 mmol, 1 equiv) was suspended in 7 mL of
 5 HCOOH and the mixture was stirring at 110 °C for 2 h. The solvent was evaporated under reduced pressure and the residue, dissolved in 7 mL of *n*-BuOH, was reacted with the ligand Hampt (100.8 mg, 0.51 mmol, 1 equiv) and the base Et₃N (1.4 mL, 10.3 mmol, 20 equiv). The mixture was stirred at 110 °C overnight, the solvent was evaporated under reduced pressure. The residue was dissolved in 2 mL of CHCl₃ and
 10 the base K₂CO₃ (320 mg, 2.32 mmol, 4.5 equiv) was added. After stirring for 2 h at room temperature, the mixture was filtrated. The filtrate was concentrated to about 1 mL and the complex was precipitated by addition of 10 mL of ethyl ether. The obtained solid was filtered, washed two times with 3 mL of ethyl ether, one time 3 mL of with *n*-pentane and dried at reduced pressure. Yield 61.2 mg (%). Anal. Calcd (%) for C₁₅H₁₃ClN₂O₂Ru: C, 46.22; H, 3.36; N, 7.19. Found: C, 46.25; H, 3.30; N, 7.01. ¹H NMR (200 MHz, CDCl₃) δ 7.82 – 7.61 (m, 2H), 7.63 – 7.45 (m, 2H), 7.07 (d, *J* = 6.9 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 4.61 (dd, *J* = 16.6, 6.7 Hz, 1H), 4.39 (dd, *J* = 17.6, 8.1 Hz, 1H), 4.20 – 4.02 (m, 1H), 3.51 – 3.28 (m, 1H), 2.30 (s, 3H). ¹³C NMR (50 MHz, CDCl₃) δ 200.4 (s, CO), 193.7 (s, CO), 163.5 (s, NCC), 162.8 (s, NCC), 157.3 (s, Cq aro), 156.27
 15 (s, Cq aro), 142.2 (s, Cq aro), 140.8 (s, C-H aro), 138.7 (s, C-H aro), 125.0 (C-H aro), 124.4 (s, C-H aro), 117.5 (s, C-H aro), 117.0 (s, C-H aro), 60.4 (s, CH₂), 21.6 (s, CH₃). IR (cm⁻¹): 2028, 1958.

Example 5: Synthesis of the complex [Ru{(2-CH₂-6-Me-C₆H₃)PPh₂}(CO)₂(en)]Cl (5)

The compound RuCl₃·xH₂O (207.9 mg, 1 mmol, 1 equiv) was suspended in 5 mL of
 25 HCOOH and the mixture was stirred in a sealed tube at 100 °C for 2 h (until the mixture became yellow and homogenous), obtaining [RuCl₂(CO)₂]_n. The solvent was evaporated under reduced pressure and the residue was dissolved in 6 mL of distilled EtOH. The solution was reacted with the ligand (2,6-Me₂C₆H₃)PPh₂ (881.9 mg, 3 mmol, 3 equiv) and Et₃N (680 μ L, 5 mmol, 5 equiv). After stirring at 80 °C overnight, the volume was
 30 reduced to about half and filtered. The solid was washed 3 times with 3 mL of EtOH, 2 times with 3 mL of ethyl ether, on time with 2 mL of *n*-pentane and dried under reduced pressure, affording the complex [RuCl{(2-CH₂-6-Me-C₆H₃)PPh₂}(CO)₂[(2,6-Me₂C₆H₃)PPh₂].

Said complex [RuCl{(2-CH₂-6-Me-C₆H₃)PPh₂}(CO)₂[(2,6-Me₂C₆H₃)PPh₂]] (252 mg, 0.33
 35 mmol, 1 equiv), suspended in 5 ml of methanol, was reacted with the ligand en (45 μ L,

0.67 mmol, 2.1 equiv) and CaCO_3 (16 mg, 0.16 mmol, 0.5 equiv). After stirring at 65 °C overnight, the mixture was filtered. The volume of the filtrate was reduced to about half, and the complex precipitated by adding 7 mL of *n*-pentane. The obtained solid was filtered and washed two times with 2 mL of ethyl ether and dried under reduced pressure. Yield 156 mg (88%). Anal. Calcd (%) for $\text{C}_{24}\text{H}_{26}\text{ClN}_2\text{O}_2\text{PRu}$: C, 53.19; H, 4.84; N, 5.17, Found: C, 53.32; H, 4.79; N, 5.02. ^1H NMR (200 MHz, CD_3OD) δ 7.61 – 7.26 (m, 12H), 6.99 (dd, J = 6.6, 3.2 Hz, 1H), 4.35 – 4.14 (m, 1H), 4.12 – 3.84 (m, 1H), 2.93 (d, J = 15.0 Hz, 1H), 2.51 (d, J = 14.9 Hz, 1H), 1.64 (s, 3H). ^{13}C NMR (50 MHz, CD_3OD) δ 201.3 (d, J = 13.5 Hz), 191.9 (d, J = 6.5 Hz), 163.3 (d, J = 33.1 Hz), 142.0 (d, J = 1.7 Hz), 136.3, 135.22, 133.4 (d, J = 10.2 Hz), 133.0 (d, J = 2.7 Hz), 132.1 (d, J = 2.5 Hz), 131.9, 131.6 (d, J = 2.4 Hz), 131.5 (d, J = 10.5 Hz), 130.7 (d, J = 10.0 Hz), 130.2 (d, J = 10.5 Hz), 129.9, 129.6, 129.2 (d, J = 6.5 Hz), 45.4 (d, J = 3.9 Hz), 31.9 (d, J = 4.1 Hz), 22.3 (d, J = 3.9 Hz). ^{31}P NMR (81 MHz, CD_3OD) δ 64.6.

Example 6: Synthesis of the complex $[\text{Ru}\{(2\text{-CH}_2\text{-6-Me-C}_6\text{H}_3)\text{PPh}_2\}(\text{CO})_2(\text{ampy})]\text{Cl}$ (6)

The complex $[\text{RuCl}\{(2\text{-CH}_2\text{-6-Me-C}_6\text{H}_3)\text{PPh}_2\}(\text{CO})_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{PPh}_2]]$ (251 mg, 0.32 mmol, 1 equiv) prepared as in Example 5, suspended in 5 mL of methanol, was reacted with ampy (68 μL , 0.66 mmol, 2.1 equiv) and CaCO_3 (16 mg, 0.16 mmol, 0.5 equiv). After stirring at 65 °C overnight, the solution was filtrated. The volume of the filtrate was reduced by about half, and the complex was precipitated by adding 7 mL of *n*-pentane. The obtained solid was filtered and washed two times with 2 mL of ethyl ether and dried under reduced pressure. Yield 83 mg (44%). Anal. Calcd (%) for $\text{C}_{28}\text{H}_{26}\text{ClN}_2\text{O}_2\text{PRu}$: C, 57.00; H, 4.44; N, 4.75, Found: C, 57.32; H, 4.24; N, 4.53. ^1H NMR (200 MHz, CD_3OD) δ 8.74 (d, J = 5.5 Hz, 1H), 7.96 (t, J = 7.3 Hz, 1H), 7.71 – 7.28 (m, 14H), 7.14 – 6.99 (m, 1H), 4.26 – 4.10 (m, 2H), 2.92 (d, J = 15.4 Hz, 1H), 2.66 (d, J = 15.4 Hz, 1H), 1.70 (s, 3H). ^{13}C NMR (50 MHz, CD_3OD) δ 201.3 (d, J = 14.6 Hz), 191.5 (d, J = 6.5 Hz), 162.8, 162.6 (d, J = 32.1 Hz), 153.7, 143.1 (d, J = 2.2 Hz), 140.3, 135.1, 133.2, 133.2 (d, J = 10.3 Hz), 132.4 (d, J = 2.5 Hz), 132.0 (d, J = 2.7 Hz), 131.8 (d, J = 10.4 Hz), 131.5, 130.9 (d, J = 10.2 Hz), 130.4 (d, J = 10.7 Hz), 129.6 (d, J = 6.4 Hz), 129.5 (d, J = 3.7 Hz), 126.3 (d, J = 2.0 Hz), 123.3 (d, J = 1.9 Hz), 52.2 (d, J = 3.4 Hz), 33.9 (d, J = 3.9 Hz), 22.3 (d, J = 3.9 Hz). ^{31}P NMR (81 MHz, CD_3OD) δ 64.4. IR (cm^{-1}): 2020, 1957.

Example 7: Synthesis of the complex $\text{RuCl}_2(\text{CO})_2[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{PPh}_2]_2$ (7)

The complex $[\text{RuCl}_2(\text{CO})_3]_2$ (50 mg, 0.1 mmol, 1 equiv) suspended in 5 mL of distilled EtOH, was reacted with the ligand $(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{PPh}_2$ (126 mg, 0.44 mmol, 4.4 equiv). After stirring at 80 °C overnight, the solvent was evaporated under reduced pressure and the residue was dissolved in 2 mL of CHCl_3 and stirred at room temperature for

further 2 h. The volume was reduced to about half and the complex was precipitated by addition of 5 mL of ethyl ether. The obtained solid was filtrated, washed 2 times with 3 mL of ethyl ether, once with 3 mL of *n*-pentane and dried under reduced pressure. Yield 133 mg (84%). Anal. Calcd (%) for $C_{42}H_{38}Cl_2O_2P_2Ru$: C, 62.38; H, 4.74, Found: C, 62.60; H, 4.98. 1H NMR (200 MHz, CD_2Cl_2) δ 7.38 – 7.18 (m, 26H), 2.12 (s, 12 H). ^{13}C NMR (50 MHz, CD_2Cl_2) δ . ^{31}P NMR (81 MHz, CD_2Cl_2) δ 10.1. IR (cm^{-1}): 2039, 2001.

Example 8: *catalytic reduction by transfer hydrogenation of ketones and aldehydes with complexes of examples 1-6.*

The catalyst solution was prepared in a 10 mL Schlenk by adding 5 mL of 2-propanol to the chosen ruthenium complex (0.02 mmol). By stirring, the complex dissolved over a period of a few minutes. Separately, in a second Schlenk (20 mL), 250 μ L of the previously prepared solution containing the catalyst and 200 μ L of a 0.1 M sodium isopropoxide solution in 2-propanol were added subsequently to the ketone or aldehyde solution (1 mmol) in 10 mL of 2-propanol under reflux.

The start of the reaction was considered to be when the base was added. The molar ratio of substrate/catalyst (S/C) varied from 1000/1 to 100000/1. The molar ratio substrate/base was in the range of 10/1 to 100/1. The reaction was performed in the range of 20 to 82 °C (boiling point of 2-propanol).

For the reactions, in which the catalyst was formed in situ, a pre-catalyst solution was prepared by adding 5 mL of 2-propanol to the pre-catalyst (0.02 mmol) and the corresponding ligand (0.1 mmol) (see Tables 2 and 3) and the solution was stirred for 30 min at reflux. The solution of the in situ formed catalyst was used in the reduction reaction as described above.

The results of the GC analysis for the reduction of acetophenone are reported in Table 2, while those for other ketones and aldehydes are shown in Table 3.

Table 2. Catalytic transfer hydrogenation of acetophenone (0.1 M) to 1-phenylethanol with the complexes 1-6 in the presence of a ligand with NaOiPr 2 mol %

Complex	S/C	Ligand	L/C	Conversion % (min)	TOF (h ⁻¹)
1	1000	PPh ₃	2	100 (60)	1000
1	1000	PCy ₃	2	100 (1)	>30000
1	50000	PCy ₃	2	100 (15)	100000
2	1000	PPh ₃		97 (60)	
2	1000	PCy ₃		96 (15)	
3	1000	PPh ₃		97 (60)	
3	1000	PCy ₃		96 (15)	
5	1000	-		13 (1)	
6	1000	-		100 (0,17)	3000

5

Table 3. Catalytic transfer hydrogenation of ketones and aldehydes (0.1 M) to alcohols with the complexes 1-3 in the presence of a ligand with NaOiPr 2 mol %

Complex	Substrate	S/C	Ligand	Conversion % (min)	TOF (h ⁻¹)
1	isobutyrophenone	10000	PCy ₃	100 (60)	1000
1	pivalophenone	10000	PCy ₃	100 (1)	>30000
1	benzophenone	10000	PCy ₃	100 (15)	100000
1	camphor	2000	PCy ₃	97 (60)	
1	pivalone	10000	PCy ₃	96 (15)	
1	cyclohexanone	10000	PCy ₃	97 (60)	
1	allylacetone	10000	PCy ₃	96 (15)	
2	benzaldehyde	1000	PPh ₃	100 (2)	12000
2	benzaldehyde	1000	PCy ₃	100 (36)	8000
3	benzaldehyde	1000	PPh ₃	100 (60)	1000
3	benzaldehyde	1000	PCy ₃	100 (1)	>30000

10

The experimental results show that with the complex **1** in the presence of PCy₃, the reduction of linear, cyclic and aryl alkyl ketones, and aldehydes to the corresponding alcohols in 2-propanol under reflux was extremely fast and was complete within a few minutes, using a substrate/catalyst ratios equal to 50000 in the case of reduction of acetophenone.

The turnover frequency values (TOF) were up to 100000 h⁻¹, depending on the steric

and electronic characteristics of the substrate (Tables 2 and 3).

Example 9: catalytic reduction of ketones with complexes of examples 1-7 using molecular hydrogen

The hydrogenation reactions were performed in an 8 vessels Endeavor Parr apparatus.

- 5 The vessels were charge with the catalysts (2.5 μmol). The vessels were closed, charged with 5 bar of N_2 and slowly vented five times. The ketone (0.6 mL, 5 mmol), optionally ligand (5 μmol), the solvent (0.9 mL of methanol or ethanol) and 1 mL of a solution of *t*-BuOK 0.1 M were added. The vessels were charged with 20 bar of H_2 and slowly vented four times. The vessel was charged to 30 bars and heated to 70 $^\circ\text{C}$. The
- 10 molar ratio of substrate/catalyst varied from 2000/1 to 25000/1. The molar ratio of substrate/base were 10/1 to 100/1. The hydrogen uptake was calculated by the apparatus and the results of the GC analysis at the end of the runs are shown in Tables 4 for the catalytic reduction of acetophenone and in Table 5 for other substrates.

15 **Table 4. Catalytic hydrogenation of acetophenone to 1-phenylethanol in the presence of the complexes 1-3, 5-7 in the presence of a ligand**

Complex	S/C	Ligand	Solvent	Base (%)	Conversion % (h)	TOF (h^{-1})
1	2000	PPh_3	EtOH	<i>t</i> -BuOK (2)	34 (16)	
1	2000	PCy_3	EtOH	<i>t</i> -BuOK (2)	46 (16)	
1	2000	PCy_3	MeOH	<i>t</i> -BuOK (5)	100 (16)	
2	2000	PCy_3	MeOH	<i>t</i> -BuOK (5)	100 (16)	
3	2000	PCy_3	MeOH	<i>t</i> -BuOK (5)	100 (16)	
5	2000	-	EtOH	<i>t</i> -BuOK (2)	100 (16)	
5	10000	-	EtOH	<i>t</i> -BuOK (2)	44 (16)	
5	2000	-	MeOH	<i>t</i> -BuOK (2)	100 (16)	
5	10000	-	MeOH	<i>t</i> -BuOK (2)	95 (3)	4450 ^a
5	25000	-	MeOH	<i>t</i> -BuOK (2)	97 (22)	3300 ^a
6	2000	-	EtOH	<i>t</i> -BuOK (2)	100 (16)	
6	10000	-	EtOH	<i>t</i> -BuOK (2)	11 (16)	
6	2000	-	MeOH	<i>t</i> -BuOK (2)	100 (16)	
6	10000	-	MeOH	<i>t</i> -BuOK (2)	99 (2)	13500 ^a
6	25000	-	MeOH	<i>t</i> -BuOK (2)	97 (22)	4000 ^a
7	2000	en	EtOH	<i>t</i> -BuOK (2)	100 (16)	
7	2000	ampy	EtOH	<i>t</i> -BuOK (2)	100 (16)	

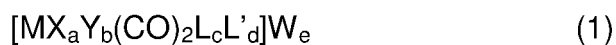
^[a] Reactions performed in 50 mL high pressure vessel (Parr autoclave)

Table 5. Catalytic hydrogenation of ketones to alcohols in the presence of the complexes 5 and 6 in ethanol with t-BuOK 2 mol %

Complex	Ketone	S/C	Conversion % (h)
5	2-octanone	1000	100 (3)
5	isobutyrophenone	1000	33 (3)
5	tetralone	10000	1 (16)
5	2'-Me-acetophenone	10000	100 (16)
5	4'-MeO-acetophenone	500	100 (3)
5	4'-NO ₂ -acetophenone	10000	2 (16)
5	benzophenone	500	100 (3)
5	benzoin	10000	9 (16)
5	2'-Cl-acetophenone	10000	100 (16)
6	2-octanone	1000	100 (3)
6	isobutyrophenone	1000	100 (3)
6	tetralone	10000	1 (16)
6	2'-Me-acetophenone	10000	100 (16)
6	4'-MeO-acetophenone	500	100 (3)
6	4'-NO ₂ -acetophenone	10000	1 (16)
6	benzophenone	500	99 (3)
6	benzoin	10000	6 (16)
6	2'-Cl-acetophenone	10000	100 (16)

CLAIMS

1. A hexacoordinate complex of Formula (1):



wherein

M = Ru or Os;

X, Y are independently selected among halides, hydride, C1-C20 carboxylates and C1-C20 alkoxides;

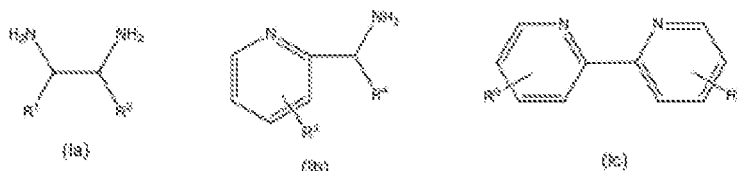
W is selected among halides, C1-C20 carboxylates and C1-C20 alkoxides;

a, b, c and e are independently 0 or 1;

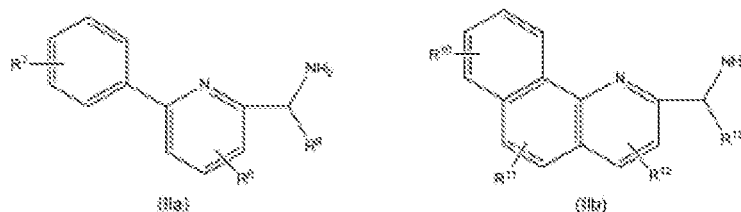
d is 0,1 or 2;

- L is a nitrogen-containing ligand selected among:

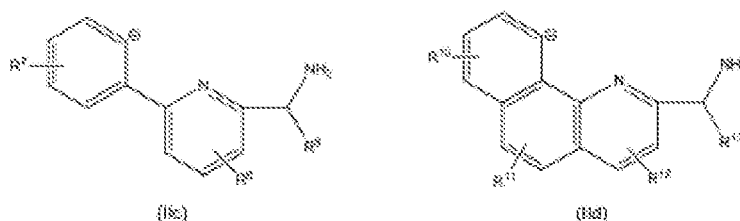
(I) a (NN) compound of formula Ia - Ic:



(II) a (HCNN) compound of formula IIa – IIb:

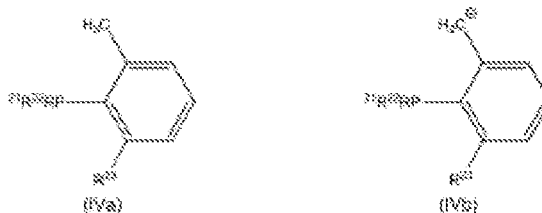


(III) a (CNN) ligand of formula IIc – IId:



wherein R¹ - R¹³ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; and

- L' is at least one phosphorus-containing ligand selected among a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



wherein

$R^{21} - R^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups;

provided that when M is Ru and

- $a = b = 1$; $c = e = 0$; $d = 2$ and $X = Y = Cl$, R^{23} is not hydrogen;

- $a = 1$; $b = c = e = 0$; $d = 2$ and $X = Cl$, HCP is not (2,6-dimethylphenyl) diphenylphosphine (Hdmpp) and CP is not the anion of (2,6-dimethylphenyl) diphenylphosphine (dmpp);

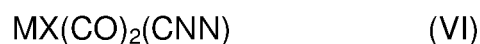
- $a = b = c = 1$; $d = e = 0$ and $X = Y = Cl$, L is not ethylenediamine or bipyridine.

2. The complex according to claim 1, of formula (V)



wherein M, X, Y and (HCNN) are as defined above.

3. The complex according to claim 1, of formula (VI)



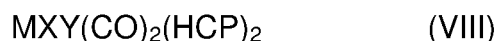
wherein M, X and (CNN) are as defined above.

4. The complex according to claim 1 of formula (VII)



wherein M, (CP), (NN) and W are as defined above.

5. The complex according to claim 1 of formula (VIII):



wherein M, X, Y and HCP are as defined above, provided that when M is Ru and $X = Y = Cl$, R^{23} is not hydrogen.

6. The complex according to claim 1 formula (IX)



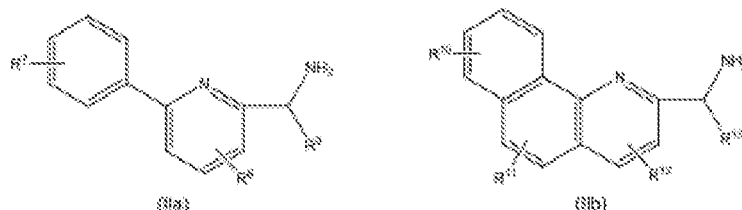
wherein M, X, CP and HCP are as defined above, provided that when M is Ru and X is Cl HCP is not (2,6-dimethylphenyl) diphenylphosphine and CP is not the anion of (2,6-dimethylphenyl) diphenylphosphine.

7. A process to obtain the complex according to any one of claims 1 to 6, comprising:

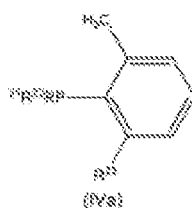
(i) reacting a compound of formula MX_2Y , wherein M, X and Y are as defined above, with HCOOH , thereby obtaining an intermediate compound of formula $[\text{MXY}(\text{CO})_2]_n$;

(ii) reacting the compound of formula $[\text{MXY}(\text{CO})_2]_n$ with at least one ligand selected among:

- a (HCNN) compound of formula IIa – IIb:



- a HCP compound of formula (IVa)



wherein

$\text{R}^7 - \text{R}^{13}$ and $\text{R}^{21} - \text{R}^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups

in the presence of a solvent and optionally of a tertiary amine of formula $\text{N}(\text{R}^{24}\text{R}^{25}\text{R}^{26})$, wherein R^{24} , R^{25} and R^{26} are independently selected among C1-C6 aliphatic groups; and

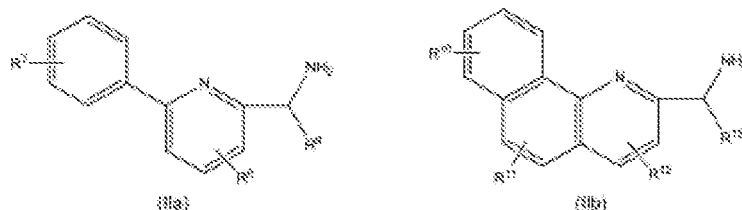
(iii) optionally reacting the compound obtained in step (ii) with a basic compound selected among potassium carbonate, calcium carbonate and mixtures thereof and/or a nitrogen-containing (NN) compound of formula Ia-Ic:



wherein $\text{R}^1 - \text{R}^6$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups.

8. The process according to claim 7 to obtain the complex of formula (V) comprising:

- (i) reacting a compound of formula MX_2Y with HCOOH , thereby obtaining an intermediate compound of formula $[\text{MXY}(\text{CO})_2]_n$;
- (ii) reacting the compound of formula $[\text{MXY}(\text{CO})_2]_n$ with a (HCNN) compound of formula IIa – IIb:

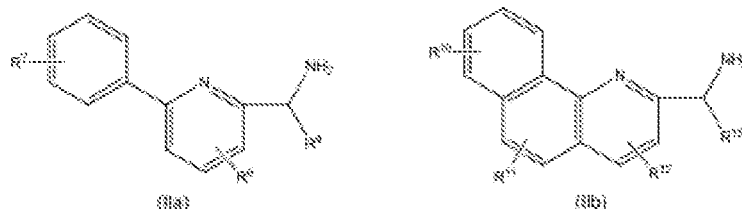


wherein

$\text{R}^7 - \text{R}^{13}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups

in the presence of a solvent.

9. The process according to claim 7 to obtain the complex of formula (VI) comprising:
- (i) reacting a compound of formula MX_2Y with HCOOH , thereby obtaining an intermediate compound of formula $[\text{MXY}(\text{CO})_2]_n$;
- (ii) reacting the compound of formula $[\text{MXY}(\text{CO})_2]_n$ with a (HCNN) compound of formula IIa – IIb:



wherein

$\text{R}^7 - \text{R}^{13}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups,

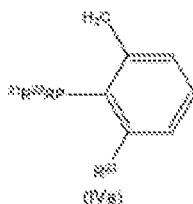
in the presence of a solvent and of a tertiary amine of formula $\text{N}(\text{R}^{24}\text{R}^{25}\text{R}^{26})$, wherein R^{24} , R^{25} and R^{26} are independently selected among C1-C6 aliphatic groups; and

(iii) reacting the compound obtained in step (ii) with a basic compound selected among potassium carbonate, calcium carbonate and mixtures thereof.

10. The process according to claim 7 to obtain the complex of formula (VII) comprising:

(i) reacting a compound of formula MX_2Y with HCOOH , thereby obtaining an intermediate compound of formula $[\text{MXY}(\text{CO})_2]_n$;

(ii) reacting the compound of formula $[MXY(CO)_2]_n$ with a (HCP) compound of formula (IVa)

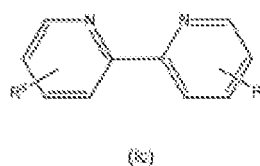
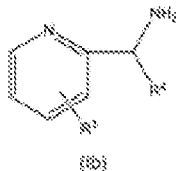
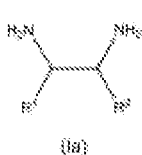


wherein

$R^{21} - R^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups

in the presence of a solvent and of a tertiary amine of formula $N(R^{24}R^{25}R^{26})$, wherein R^{24} , R^{25} and R^{26} are independently selected among C1-C6 aliphatic groups; and

(iii) reacting the compound obtained in step (ii) with a basic compound selected among potassium carbonate, calcium carbonate and mixtures thereof and a nitrogen-containing (NN) compound of formula Ia-Ic:

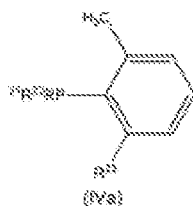


wherein $R^1 - R^6$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups.

11. The process according to claim 7 to obtain a complex of formula (VIII) comprising:

(i) reacting a compound of formula MX_2Y with $HCOOH$, thereby obtaining an intermediate compound of formula $[MXY(CO)_2]_n$;

(ii) reacting the compound of formula $[MXY(CO)_2]_n$ with at least one (HCP) compound of formula (IVa)

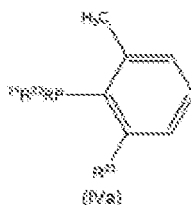


wherein

$R^{21} - R^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups
in the presence of a solvent.

12. The process according to claim 7 to obtain the complex of formula (IX) comprising:

- (i) reacting a compound of formula MX_2Y with $HCOOH$, thereby obtaining an intermediate compound of formula $[MXY(CO)_2]_n$;
(ii) reacting the compound of formula $[MXY(CO)_2]_n$ with at least one (HCP) compound of formula (IVa)



wherein

$R^{21} - R^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups,

in the presence of a solvent and of a tertiary amine of formula $N(R^{24}R^{25}R^{26})$, wherein R^{24} , R^{25} and R^{26} are independently selected among C1-C6 aliphatic group;

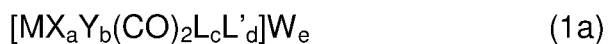
- (iii) reacting the pentacoordinate complex of formula $RuCl(CO)((2,6\text{-dimethylphenyl})dicyclohexylphosphine)((2\text{-CH}_2\text{-6-Me-C}_6\text{H}_3)dicyclohexyl\ phosphine)$ with carbon monoxide in the presence of a solvent, preferably CH_2Cl_2 .

13. Use of a compound according to any one of claims 1 to 6 as catalyst or pre-catalyst in the reduction of ketones or aldehydes to alcohols by transfer hydrogenation or hydrogenation with molecular hydrogen.

14. A process for the reduction of ketones or aldehydes to the corresponding alcohols comprising the following steps:

- (a) mixing a catalyst or pre-catalyst with a solution comprising at least one base and at least one substrate selected among C3-C42 ketones and C2-C41 aldehydes thereby obtaining a mixture; and
(b) contacting said mixture with molecular hydrogen or with at least one hydrogen-donor, preferably selected among 2-propanol, sodium formate, ammonium formate, and a mixture of formic acid and triethylamine,

said process being characterized in that the catalyst or pre-catalyst is a hexacoordinate complex of Formula (1a):



wherein

M = Ru or Os;

X, Y are independently selected among halides, hydride, C1-C20 carboxylates and C1-C20 alkoxides,

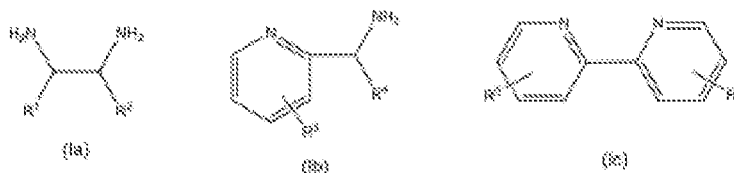
W is selected among halides, C1-C20 carboxylates and C1-C20 alkoxides;

a, b, c and e are independently 0 or 1;

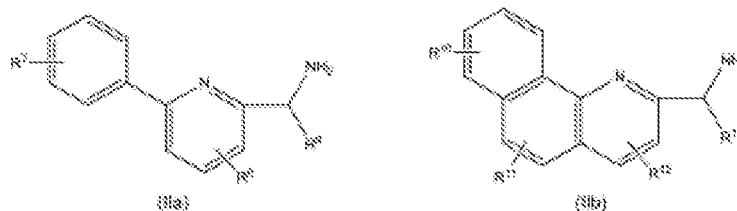
d is 0, 1 or 2;

- L is a nitrogen-containing ligand selected among:

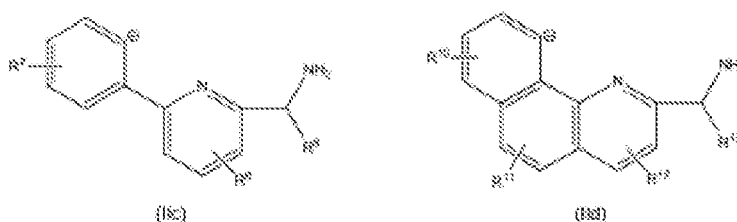
(I) a (NN) compound of formula Ia - Ic:



(II) a (HCNN) compound of formula IIa – IIb:



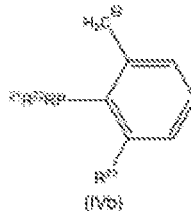
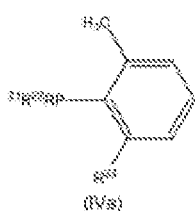
(III) a (CNN) ligand of formula IIc – IId:



wherein

R¹ - R¹³ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; and

- L' is at least one phosphorus-containing ligand selected among a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



wherein

$R^{21} - R^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups,

provided that when M is Ru and $a = 1$; $b = c = e = 0$; $d = 2$ and $X = Cl$, HCP is not (2,6-dimethylphenyl) diphenylphosphine and CP is not the anion of (2,6-dimethylphenyl) diphenylphosphine.

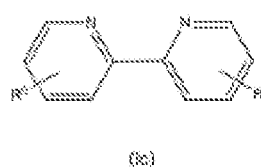
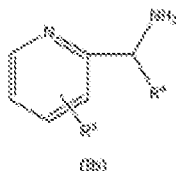
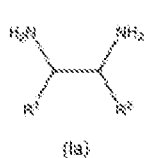
15. The process according to claim 14, comprising the following steps:

(a) mixing a pre-catalyst complex of formula (2) with a solution comprising:

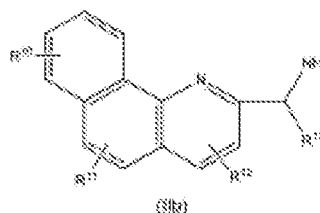
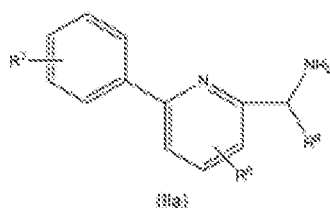
- at least one base and at least one substrate selected among C3-C42 ketones and C2-C41 aldehydes; and

- at least one nitrogen-containing compound L selected among:

(I) a NN compound of formula Ia to Ic:



(II) a HCNN compound of formula IIa – IIb:



wherein

$R^1 - R^{13}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, thereby obtaining a mixture and

(b) contacting said mixture with molecular hydrogen or with at least one hydrogen-donor, preferably selected among 2-propanol, sodium formate, ammonium formate, formic acid and triethylamine,

wherein said pre-catalyst has formula (2):



wherein

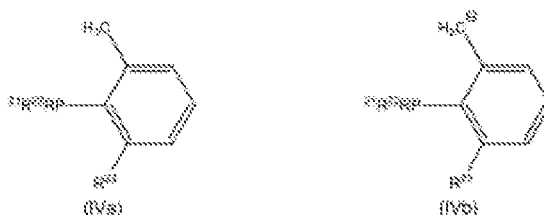
M = Ru or Os;

X and Y are independently selected among halides, hydride, C1-C20 carboxylates and C1-C20 alkoxides;

a and b are independently 0 or 1;

d is 1 or 2;

- L' is at least one phosphorus-containing ligand selected among a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



wherein

$\text{R}^{21} - \text{R}^{23}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups,

provided that

when M is Ru and $a = 1$; $b = 0$; $d = 2$ and $X = \text{Cl}$, HCP is not (2,6-dimethylphenyl) diphenylphosphine and CP is not the anion of (2,6-dimethylphenyl) diphenylphosphine.

16. The process according to claim 14, comprising the following steps:

(a) mixing a pre-catalyst complex of formula (3) with a solution comprising:

- at least one base and at least one substrate selected from the group consisting of C3-C42 ketones and C2-C41 aldehydes

- at least one phosphorus-containing compound L' selected among:

(i) a phosphine (P) selected among:

- a phosphine of formula $\text{PR}^{16}\text{R}^{17}\text{R}^{18}$, wherein $\text{R}^{16} - \text{R}^{18}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups;

- an optically active phosphine selected among (S)-neomenthyldiphenylphosphine and (R)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl;

(ii) a diphosphine (PP) selected among:

- a diphosphine of formula $\text{P}(\text{R}^{19})_2 - \text{Z} - \text{P}(\text{R}^{20})_2$, wherein Z is a C2-C4 hydrocarbon chain or ferrocene optionally substituted with C1-C20 aliphatic

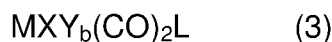
groups, and wherein R^{19} and R^{20} are independently selected among C1-C20 aliphatic groups and C5-C20 aromatic groups;

- an optically active diphosphine selected from the group consisting of (R)-(6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine), (R)-(1,1'-binaphthalene-2,2'-diyl)bis(diphenylphosphine), (R)-(1,1'-binaphthalene-2,2'-diyl)bis[bis(3,5-dimethylmethyl)phosphine], (R)-1-{2-[diphenylphosphine]ferrocenyl}ethyldicyclohexyl phosphine, (R)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethyldicyclohexyl phosphine and (2R,4R)-2,4-bis(diphenylphosphine)pentane,

thereby obtaining a mixture; and

(b) contacting said mixture with molecular hydrogen or with at least one hydrogen-donor, preferably selected among 2-propanol, sodium formate, ammonium formate, formic acid and triethylamine,

wherein said pre-catalyst has formula (3)



wherein

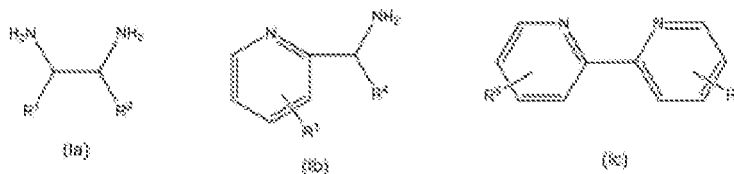
M = Ru or Os;

X and Y are independently selected among halides, hydride, C1-C20 carboxylates and C1-C20 alkoxides;

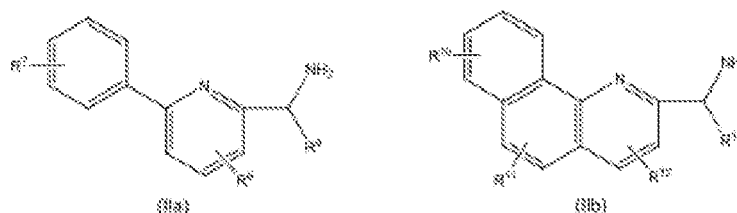
b is 0 or 1;

- L is a nitrogen-containing ligand selected among:

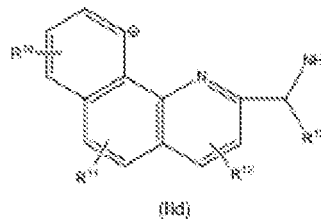
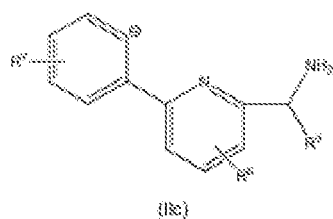
(I) a (NN) compound of formula Ia - Ic:



(II) a (HCNN) compound of formula IIa – IIb:



(III) a (CNN) ligand of formula IIc-IId:



wherein $R^1 - R^{13}$ are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups.

17. The process according to any one of claims 14 to 16, wherein in step (a) the base is an alkali metal alkoxide, preferably selected among sodium iso-propoxide, potassium tert-butoxide, potassium hydroxide, potassium carbonate, more preferably is potassium tert-butoxide.
18. The process according to any one of claims 14 to 17, wherein in step (a) the base is sodium iso-propoxide and in step (b) the mixture is contacted with at least one hydrogen donor.
19. The process according to any one of claims 14 to 18, wherein the molar ratio substrate/catalyst or pre-catalyst ranges from 1000/1 to 100000/1, preferably from 1000/1 to 50000/1.
20. The process according to any one of claims 14 to 19, wherein the molar ratio substrate/base ranges from 20 to 50.

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2017/050600

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07B41/02 C07F15/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07B C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>MORENO M A ET AL: "Synthesis, characterization, reactivity and theoretical studies of ruthenium carbonyl complexes containing ortho-substituted triphenyl phosphanes", JOURNAL OF ORGANOMETALLIC CHEMISTRY, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 690, no. 16, 15 August 2005 (2005-08-15), pages 3803-3814, XP027708946, ISSN: 0022-328X [retrieved on 2005-08-15] complexes 6,7</p> <p style="text-align: center;">----- -/-</p>	1,5



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 March 2017

Date of mailing of the international search report

17/03/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Diederer, Jeroen

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/050600

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PETER JOHN: "Strukturbestimmung isomerer Rutheniumverbindungen des Typs Ru(CO) ₂ L ₂ X ₂ durch Infrarot ([nu]CO)- und Dipolmoment-Messungen", CHEMISCHE BERICHTE, vol. 103, no. 7, 1 July 1970 (1970-07-01), pages 2178-2196, XP055298454, DE ISSN: 0009-2940, DOI: 10.1002/cber.19701030723 table 5 entry 7 (edm)RuX ₂ (CO) ₂ , X=Br, I -----	1
A	WO 2005/051965 A2 (UNIV DEGLI STUDI UDINE [IT]; BARATTA WALTER [IT]; DA ROS PAOLO [IT]; T) 9 June 2005 (2005-06-09) cited in the application compound 5, page 7 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2017/050600

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005051965	A2	09-06-2005	NONE
