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- (71) **Applicants:** UNIVERSITA' DEGLI STUDI DI UDINE [IT/IT]; Via Palladio 8, 33100 Udine (IT). INNOVATION FACTORY S.R.L. [IT/IT]; Località Padriciano 99, 34149 Trieste (IT).
- (72) **Inventors:** BARATTA, Walter; Via Freschi 7/A, 33100 Udine (IT). BALDINO, Salvatore; Via Mosca 37, 07100 Sassari (IT). GIBOULOT, Steven; 5, Boulevard des Fe-libres, 83120 Sainte-Maxime (FR).
- (74) **Agents:** ROSSETTI, Elena et al.; c/o Bugnion S.p.A., Viale Lancetti 17, 20158 Milano (IT).

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(54) **Title:** MONOCARBONYL RUTHENIUM AND OSMIUM CATALYSTS

(57) **Abstract:** The invention relates to monocarbonyl complexes of ruthenium and osmium with bi- and tridentate nitrogen and phosphine ligands. The invention 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.

**“MONOCARBONYL RUTHENIUM AND OSMIUM CATALYSTS”**

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**DESCRIZIONE**

The invention relates to monocarbonyl complexes of ruthenium and osmium with bi- and tridentate nitrogen and phosphine ligands. The invention 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 hydrogen donor molecules (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 reactions.

Recently, the complexes *trans*- $\text{RuCl}_2(\text{CO})(\text{NN})(\text{PR}_3)$  (R = Ph, p-tolyl; NN = ethylenediamine, 2-aminomethylpyridine and bipyridine) were isolated and they were found active in the transfer hydrogenation of ketones (D. A. Cavarzan et al., *Polyhedron* 2013, 62, 75). It is worth noting that the carbonyl complexes  $[\text{RuX}(\text{CO})(\text{NN})(\text{PP})]\text{Cl}$  (X =

Cl, H; NN = ethylenediamine or 2-aminomethylpyridine) and RuCl(CP)(CO)(NN) containing a cyclometallated phosphine (CP) isolated by Baratta and co-workers display high catalytic activity in the transfer hydrogenation of ketones (S. Zhang et al., *Organometallics* 2013, 32, 5299; W. Baratta et al., *Angew. Chem. Int. Ed.* 2004, 43, 3584; W. Baratta et al., *Organometallics* 2004, 23, 6264 and WO2005/051965). Complexes of the formula RuCl<sub>2</sub>(CO)(dmf)(PP) have been found active in hydrogenation, transfer hydrogenation, hydroformylation and carbonylation reactions (WO2012/123761 A1).

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 stereoselectivity is a crucial issue. Furthermore, the catalysts have to display high productivity and should be easily prepared from commercial 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 a CO ligand in combination with bidentate and tridentate nitrogen ligands and achiral or chiral phosphines. These complexes can be used as catalysts in the (asymmetric) 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 monocarbonyl complexes of ruthenium and osmium, containing nitrogen and phosphine ligands, the solution for obtaining catalysts with high catalytic activity in hydrogenation reactions with molecular hydrogen and transfer hydrogenation of carbonyl compounds to alcohols.

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



wherein

M = Ru or Os;

a, b and d are independently 0 or 1;

5 c is 1 or 2;

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

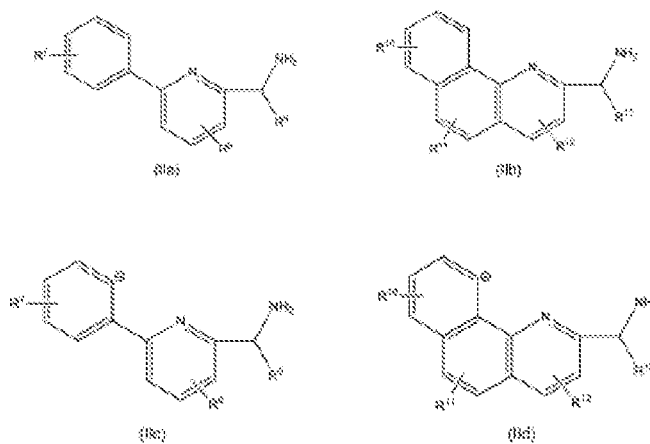
W is selected among halides, C1-C20 carboxylates and C1-C20 alkoxides;

L is a nitrogen-containing ligand selected among:

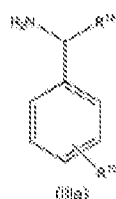
10 (I) a NN compound of formula Ia to Ic:



(II) a HCNN compound of formula IIa – IIb and a CNN ligand of formula IIc – IId:



15 (III) a HCN compound of formula IIIa

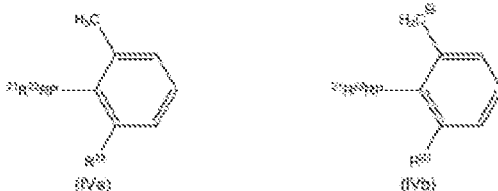


wherein

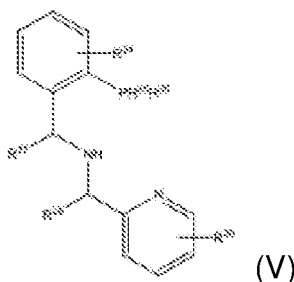
R<sup>1</sup> - R<sup>15</sup> are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups;

20 L' is at least one phosphorus-containing ligand selected among:

- a phosphine (P) selected among: a phosphine of formula  $PR^{16}R^{17}R^{18}$ , wherein  $R^{16}$  -  $R^{18}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; an optically active phosphine selected among (S)-neomenthylidiphenylphosphine and (R)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-
- 5 binaphthyl;
- a diphosphine (PP) selected among: a diphosphine of formula  $P(R^{19})_2 - Z - P(R^{20})_2$ , wherein Z is a C2-C4 aliphatic group 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
- 10 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}ethylcyclohexyl phosphine, (R)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethylcyclohexyl phosphine and (2R,4R)-2,4-
- 15 bis(diphenylphosphine)pentane;
- a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



- a PNN compound of formula (V)



- 20 wherein
- $R^{21}$  -  $R^{29}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups;
- provided that:
- when  $a = b = c = 1$ ;  $d = 0$ ;  $X = Y = Cl$ ; L is ethylenediamine or 2-(aminomethyl)pyridine
- 25 or 2,2'-bipyridine or 4,4'-dimethyl-2,2'-bipyridine, L' is not a phosphine (P) of formula  $PR^{16}R^{17}R^{18}$  in which  $R^{16} = R^{17} = R^{18} = \text{phenyl or } p\text{-tolyl}$ ;

- when  $a = 0$ ;  $b = c = d = 1$ ;  $X = W = \text{Cl}$  or  $X = \text{H}$  and  $W = \text{Cl}$ ,  $L = \text{ethylenediamine}$  or  $2\text{-(aminomethyl)pyridine}$ ,  $L'$  is not  $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{PPh}_2$ ;
- when  $a = d = 0$ ;  $b = c = 1$ ;  $X = \text{Cl}$ ;  $L = \text{ethylenediamine}$  or  $2\text{-(aminomethyl)pyridine}$ ,  $L'$  is not a ligand (CP) of formula (IVb) in which  $R^{21} = R^{22} = \text{phenyl}$  and  $R^{23} = \text{methyl}$ ; and
- 5 - when  $a, b$  and  $d$  are 0,  $c$  is 2,  $X$  is Cl and  $R^{23}$  is  $-\text{CH}_3$ ,  $R^{21}$  and  $R^{22}$  are not phenyl groups.

In a further aspect, the present disclosure refers to the use of said ruthenium or osmium complexes as catalyst 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 hydrocarbons, excluding aromatic groups.

- 10 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  $-\text{OR}$ ,  $-\text{NRR}'$ ,  $-\text{NRCOR}'$ ,  $-\text{NO}_2$ ,  $-\text{NH}_2$ ,  $-\text{COR}$ ,  $-\text{COOR}$ ,  $-\text{CONRR}'$  and halides, wherein  $R$  and  $R'$  are equal or different and can be a H or a C1-C20 aliphatic or aromatic group.

- 15 As used therein, "aromatic group" also include aromatic compounds substituted with aliphatic groups.

- As used therein, "substituted aromatic group" refers to an aromatic group in which at least one aromatic hydrogen atom is replaced with at least one substituent group selected among  $-\text{R}$ ,  $-\text{OR}$ ,  $-\text{NRR}'$ ,  $-\text{NRCOR}'$ ,  $-\text{NO}_2$ ,  $-\text{NH}_2$ ,  $-\text{COR}$ ,  $-\text{COOR}$ ,  $-\text{CONRR}'$  and halides, wherein  $R$  and  $R'$  are equal or different and can be a H or a C1-C20 aliphatic or
- 20 aromatic group.

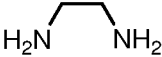
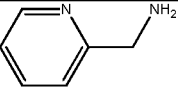
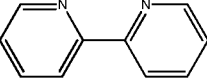
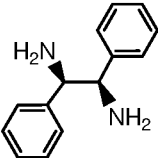
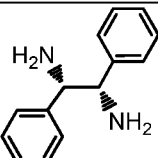
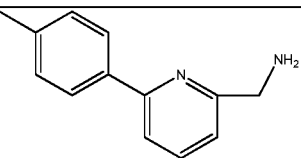
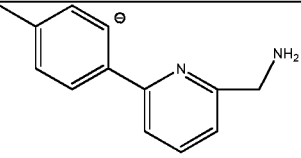
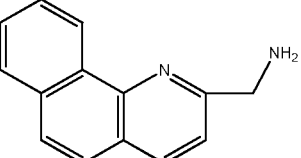
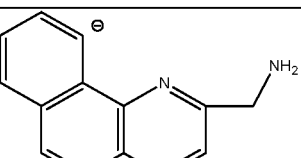
As used therein, "heteroaromatic group" refers to aromatic groups in which at least one carbon atom which is part of the aromatic ring is replaced with one heteroatom selected among N, S, O and P.

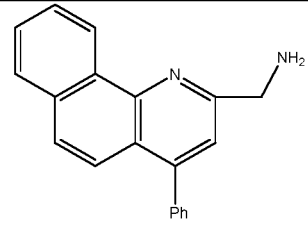
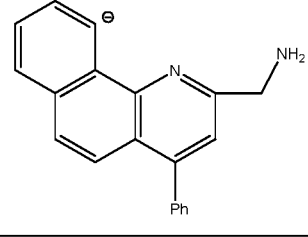
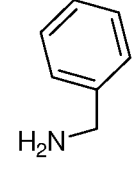
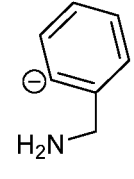
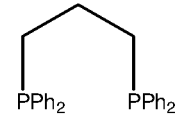
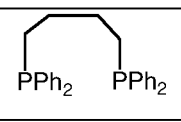
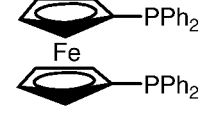
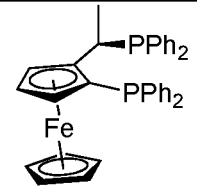
- 25 As used therein, "hydrogen-donor" refers to a compound that transfers a hydrogen atom to another compound.

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

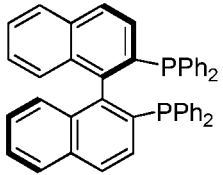
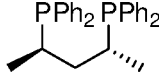
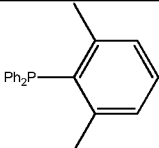
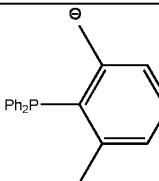
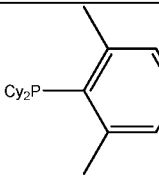
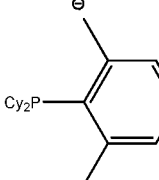
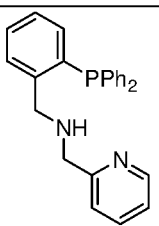
In the present description and appended claims the abbreviations listed in Table 1 are used:

**Table 1. Abbreviation of the nitrogen and phosphorus ligands**

<b>Chemical name</b>	<b>Abbreviation</b>	<b>Structural formula</b>
<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 <sup>Ph</sup>	
Anionic form of 4-phenyl-2-(aminomethyl)benzo[ <i>h</i> ]quinoline	ambq <sup>Ph</sup>	
benzylamine	H <sub>2</sub> CN	
Anionic form of benzylamine	CN	
<i>phosphorus-containing ligand L'</i>		
triphenylphosphine	PPh <sub>3</sub>	
tricyclohexylphosphine	PCy <sub>3</sub>	
triisopropylphosphine	P <i>i</i> Pr <sub>3</sub>	
1,3-bis(diphenylphosphino)propane	dppp	
1,4-bis(diphenylphosphino)butane	dppb	
1,1'-bis(diphenylphosphino)ferrocene	dppf	
( <i>R</i> )-1-[( <i>S<sub>P</sub></i> )-2-(diphenylphosphino)ferrocenylethyl]diphenylphosphine	( <i>R</i> )-Josiphos	



( <i>R</i> )-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene	( <i>R</i> )-BINAP	
( <i>R,R</i> )-Skewphos	( <i>R,R</i> )-BDPP	
(2,6-dimethylphenyl)diphenylphosphine	Hdmpp	
Anionic form of (2,6-dimethylphenyl)diphenylphosphine	dmpp	
(2,6-dimethylphenyl)dicyclohexyl phosphine	Hdmppc	
Anionic form of (2,6-dimethylphenyl)dicyclohexyl phosphine	dmppc	
	PNN	

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

5



wherein

M = Ru or Os;

a, b and d are independently 0 or 1;

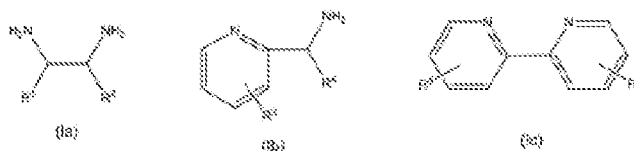
c is 1 or 2;

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

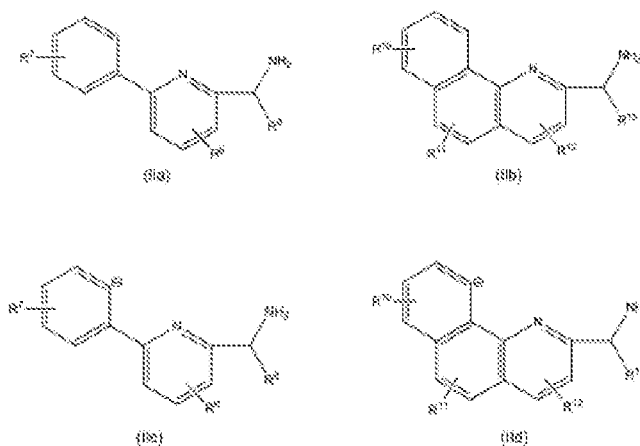
W is selected among halides, C1-C20 carboxylates and C1-C20 alkoxides;

L is a nitrogen-containing ligand selected among:

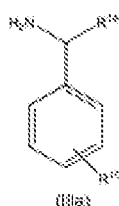
- 5 (I) a NN compound of formula Ia to Ic:



- (II) a HCNN compound of formula IIa – IIb and a CNN ligand of formula IIc – IId:



- 10 (III) a HCN compound of formula IIIa



wherein

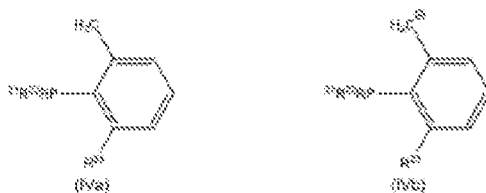
- 15 R<sup>1</sup> - R<sup>15</sup> are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R<sup>1</sup> and R<sup>2</sup> may be independently selected among H and a phenyl group and/or R<sup>3</sup>-R<sup>6</sup> and R<sup>8</sup>-R<sup>15</sup> may be H and/or R<sup>7</sup> may be 4-methyl;

L' is at least one phosphorus-containing ligand selected among:

- a phosphine (P) selected among: a phosphine of formula PR<sup>16</sup>R<sup>17</sup>R<sup>18</sup>, wherein R<sup>16</sup> - R<sup>18</sup> are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; an optically active phosphine selected among (S)-

neomenthylidiphenylphosphine and (*R*)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl;

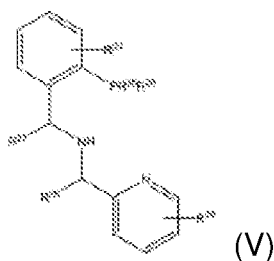
- a diphosphine (PP) selected among: a diphosphine of formula  $P(R^{19})_2 - Z - P(R^{20})_2$ , wherein Z is a C2-C4 aliphatic group or ferrocene optionally substituted with C1-C20 aliphatic groups, and wherein  $R^{19}$  and  $R^{20}$  are independently selected among C1-C20 aliphatic groups and C5-C20 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}ethylidicyclohexyl phosphine, (*R*)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethylidicyclohexyl phosphine and (2*R*,4*R*)-2,4-bis(diphenylphosphine)pentane;
- a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



15 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  $-CH_3$  and/or  $R^{21} - R^{22}$  may be independently selected among phenyl and cyclohexyl group

20 - a PNN compound of formula (V)



wherein

$R^{24} - R^{29}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably  $R^{24}$  and  $R^{27} - R^{29}$  may be H and/or  $R^{25}$  and  $R^{26}$  may be a C1-

25 C20 aromatic group, more preferably a phenyl group;

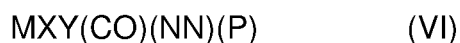
provided that:

- when  $a = b = c = 1$ ;  $d = 0$ ;  $X = Y = \text{Cl}$ ; L is ethylenediamine or 2-(aminomethyl)pyridine or 2,2'-bipyridine or 4,4'-dimethyl-2,2'-bipyridine, L' is not a phosphine (P) of formula  $\text{PR}^{16}\text{R}^{17}\text{R}^{18}$  in which  $\text{R}^{16} = \text{R}^{17} = \text{R}^{18} = \text{phenyl}$  or *p*-tolyl;
  - when  $a = 0$ ;  $b = c = d = 1$ ;  $X = W = \text{Cl}$  or  $X = \text{H}$  and  $W = \text{Cl}$ , L = ethylenediamine or 2-(aminomethyl)pyridine, L' is not  $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{PPh}_2$ ;
  - when  $a = d = 0$ ;  $b = c = 1$ ;  $X = \text{Cl}$ ; L = ethylenediamine or 2-(aminomethyl)pyridine, L' is not a ligand (CP) of formula (IVb) in which  $\text{R}^{21} = \text{R}^{22} = \text{phenyl}$  and  $\text{R}^{23} = \text{methyl}$ ; and
  - when a, b and d are 0, c is 2, X is Cl and  $\text{R}^{23}$  is  $-\text{CH}_3$ ,  $\text{R}^{21}$  and  $\text{R}^{22}$  are not phenyl groups.
- 10 In complexes of formula (1), when  $c = 2$  and L' represents two phosphorus-containing ligands independently selected among the phosphorus-containing compounds listed above, when one L' is CP and one L' is HCP, the complex of formula (1) is pentacoordinate complex.

The high modularity of the nitrogen-containing ligands (Ia-c), (IIa-d) and (IIIa) in combination with phosphines (P), diphosphines (PP), HCP phosphines and PNN phosphines, 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 X, Y, W, L, and L', the complexes of sub-formulas (VI – XIV) given below may be obtained, which are encompassed by the general formula (1).

According to an embodiment, the bidentate (NN) ligands of type (Ia-c) have the ability, through the nitrogen atoms of a  $-\text{NH}_2$  group or of a heterocycle in combination with monodentate phosphines, to coordinate the metal. Thus, the present disclosure may refer to a complex of formula (VI)



wherein M, X, Y, (NN) and (P) are as defined above, provided that when X and Y are Cl,  $\text{R}^{16} - \text{R}^{18}$  are not phenyl or *p*-tolyl groups.

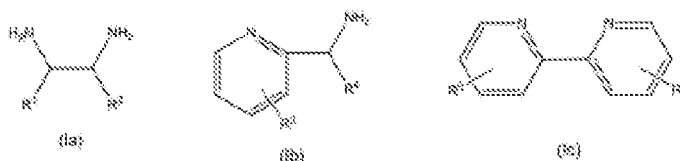
According to a specific embodiment, the present disclosure may refer to complexes of formula (VI) wherein M, X, Y, (NN) and (P) are as defined above, provided that when X and Y are Cl,  $\text{R}^{16} - \text{R}^{18}$  are not aromatic groups.

- 15 Complexes of formula (VI) can be obtained as a mixture of *trans*-isomers (eg. complex **4** and **6** below) and *cis*-isomers (eg. complex **5** and **7**).

The present disclosure also refers to a process to obtain complexes of formula (VI) comprising reacting a compound of formula  $\text{MXY}(\text{CO})(\text{PPh}_3)_2$ , or of formula

MXY(CO)(PPh<sub>3</sub>)<sub>2</sub>(dmf), wherein M, X, Y are as defined above and (dmf) is dimethylformamide, with a phosphine (P) selected among:

- phosphines of formula PR<sup>16</sup>R<sup>17</sup>R<sup>18</sup>, wherein R<sup>16</sup> - R<sup>18</sup> are independently selected among H, C1-C20 aliphatic group and C5-C20 aromatic groups; and
  - 5 - an optically active phosphine selected among (*S*)-neomenthyl-diphenylphosphine and (*R*)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl;
- and at least one nitrogen-containing compound NN selected among



wherein

R<sup>1</sup> - R<sup>6</sup> are independently selected among H, C1-C20 aliphatic group and C5-C20 aromatic group, preferably R<sup>1</sup> and R<sup>2</sup> may be independently selected among H and a phenyl group and/or R<sup>3</sup>-R<sup>6</sup> may be H. Compounds of formula MXY(CO)(PPh<sub>3</sub>)<sub>2</sub> or of formula MXY(CO)(PPh<sub>3</sub>)<sub>2</sub>(dmf) may be prepared by reacting compounds of formula MXY(PPh<sub>3</sub>)<sub>k</sub>, wherein k is 2 or 3 with carbon monoxide, in the presence of a suitable organic solvent and optionally of dimethylformamide.

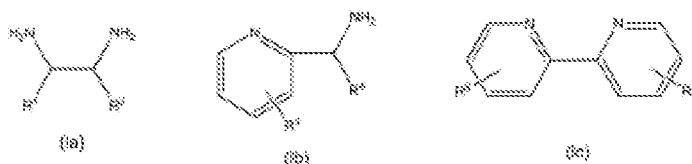
According to an embodiment, when X = Y = Cl, the compound MCl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>(dmf) may be formed by reacting MCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> with CO in the presence of dimethylformamide and a suitable organic solvent. When M is Ru, the compound RuCl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>(dmf) may be formed by reacting RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> with CO in the presence of dimethylformamide and a suitable organic solvent.

- 10 According to an embodiment, when X = Y = acetate (OAc), the compound M(OAc)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> may be formed by reacting M(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> with CO in the presence of a suitable organic solvent. When M is Ru, the compound Ru(OAc)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> may be formed by reacting Ru(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> with CO in the presence of a suitable organic solvent.

- 15 Compounds such as RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and Ru(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> are commercially available.

According to a preferred embodiment, the present disclosure may refer to a process to obtain a complex of formula (VI) wherein M is Ru and X=Y= Cl or acetate (OAc), by reacting RuCl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>(dmf) or Ru(OAc)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> with a phosphine (P) selected among:

- a phosphine of formula  $PR^{16}R^{17}R^{18}$ , wherein  $R^{16} - R^{18}$  are independently selected among H, C1-C20 aliphatic group and C5-C20 aromatic groups; and an optically active phosphine selected among (*S*)-neomenthylidiphenylphosphine and (*R*)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl;
- 5 and at least one nitrogen-containing compound NN selected among

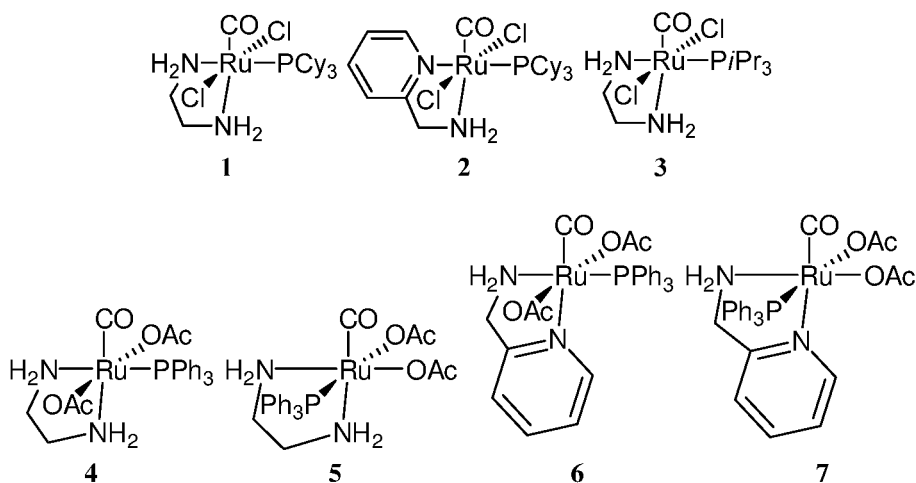


wherein

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

According to a further embodiment, the present disclosure may refer to a process to obtain complexes of formula (VI) with the limitations described above.

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



- 10 The synthesis of the monocarbonyl complexes **1-3** involves the use of *t,t,t*- $RuCl_2(CO)(dmf)(PPh_3)_2$  as starting product which can be prepared by reaction between the commercially available compound  $RuCl_2(PPh_3)_3$  with CO in dimethylformamide (dmf). The complex **1** was obtained by reacting  $RuCl_2(CO)(dmf)(PPh_3)_2$  with  $PCy_3$  via the mixed phosphine intermediate  $RuCl_2(CO)(dmf)(PPh_3)(PCy_3)$  in  $CH_2Cl_2$  and further
- 15 addition of ethylenediamine, whereas reaction with 2-(aminomethyl)pyridine, in place of ethylenediamine, gave complex **2**. Similarly, complex **3** was prepared using  $PiPr_3$ , in place of  $PCy_3$ , with ethylenediamine.

Similarly the complexes **4-7** of the invention were prepared from  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  as starting product, which can be easily prepared on gram-scale by reaction between  $\text{Ru}(\text{OAc})_2(\text{PPh}_3)_2$  with CO in MeOH. The complexes **4** and **5** were obtained as a mixture by reacting  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  with the ligand ethylenediamine in  $\text{CH}_2\text{Cl}_2$ , whereas  
 5 reaction with 2-(aminomethyl)pyridine, in place of ethylenediamine, gave complexes **6** and **7** in a similar ratio of isomer (about 2/3, in favour of the *cis*-OAc isomers).

The activity in transfer hydrogenation of complex **2** is higher than that of complexes known in the art, such as  $\text{RuCl}_2(\text{CO})(\text{ampy})(\text{PPh}_3)$ , reported by Cavarzan et al. (*Polyhedron* 2013, 62, 75), since the presence of the more basic phosphine allows the  
 10 reduction at lower catalyst loading (S/C 5000 vs. 500).

According to an embodiment, the present disclosure may refer to a complex of formula (VII)



wherein M, X, W, (NN) and (PP) are as defined above and provided that when X is Cl or  
 15 H, (NN) is not ethylenediamine or 2-(aminomethyl)pyridine and the diphosphine (PP) is not  $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{PPh}_2$ .

According to a specific embodiment, the present disclosure may refer to complexes of formula (VII) wherein M, X, and (NN) are as defined above, provided that when X is Cl or H, the diphosphine (PP) may be selected among:

- 20 - ferrocene optionally substituted with C1-C20 aliphatic 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}ethyl dicyclohexyl  
 25 phosphine, (*R*)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethyl dicyclohexyl phosphine and (2*R*,4*R*)-2,4-bis(diphenylphosphine)pentane.

The present disclosure also refers to a process to obtain complexes of formula (VII) comprising reacting  $[\text{MXY}(\text{CO})_2]_n$ ,  $\text{MXY}(\text{CO})(\text{PPh}_3)_2$  or  $\text{MXY}(\text{CO})(\text{PPh}_3)_2(\text{dmf})$ , wherein  
 30 M, X and Y are as defined above and (dmf) is dimethylformamide, with 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 aliphatic group or ferrocene, optionally substituted with C1-C20 aliphatic groups, and wherein  $\text{R}^{19}$

and R<sup>20</sup> are independently selected among C1-C20 aliphatic groups and C5-C20 aromatic groups; and

- 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}ethylcyclohexyl phosphine, (*R*)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethylcyclohexyl phosphine and (*2R,4R*)-2,4-bis(diphenylphosphine)pentane;

and at least one nitrogen-containing compound NN selected among:



wherein

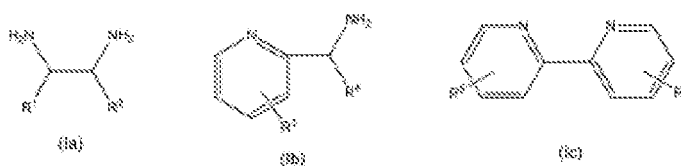
R<sup>1</sup> – R<sup>6</sup> are independently selected among H, C1-C20 aliphatic group and C5-C20 aromatic group, preferably R<sup>1</sup> and R<sup>2</sup> may be independently selected among H and a phenyl group and/or R<sup>3</sup>-R<sup>6</sup> may be H.

According to a preferred embodiment, the present disclosure may refer to a process to obtain a complex of formula (VII) wherein M is Ru and X=Y= Cl or acetate (OAc), by reacting [RuCl<sub>2</sub>(CO)<sub>2</sub>]<sub>n</sub> or RuCl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>(dmf) or Ru(OAc)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> with a diphosphine (PP) selected among:

- a diphosphine of formula P(R<sup>19</sup>)<sub>2</sub>-Z-P(R<sup>20</sup>)<sub>2</sub>, wherein Z is a C2-C4 aliphatic group or ferrocene, optionally substituted with C1-C20 aliphatic groups, wherein R<sup>19</sup> and R<sup>20</sup> are independently selected among C1-C20 aliphatic groups and C5-C20 aromatic groups; and
- 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}ethylcyclohexyl phosphine, (*R*)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethylcyclohexyl phosphine and (*2R,4R*)-2,4-bis(diphenylphosphine)pentane;

and at least one nitrogen-containing compound NN selected among:





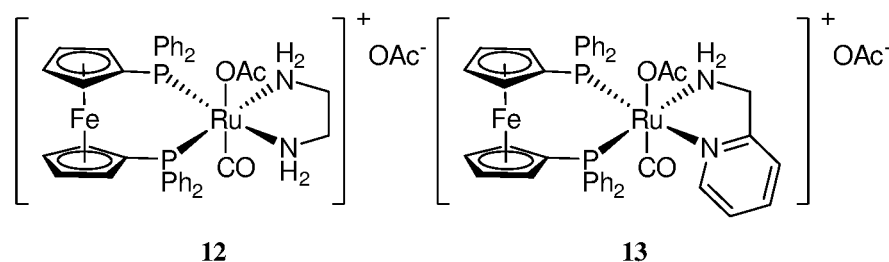
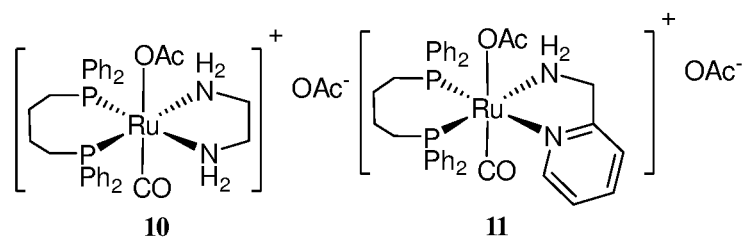
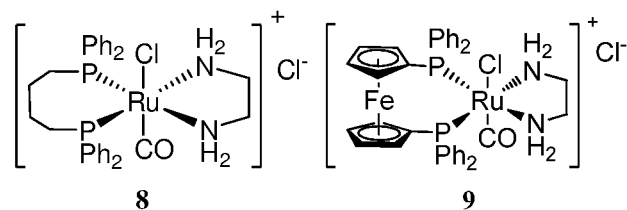
wherein

R<sup>1</sup> – R<sup>6</sup> are independently selected among H, C1-C20 aliphatic group and C5-C20 aromatic group, preferably R<sup>1</sup> and R<sup>2</sup> may be independently selected among H and a phenyl group and/or R<sup>3</sup>-R<sup>6</sup> may be H.

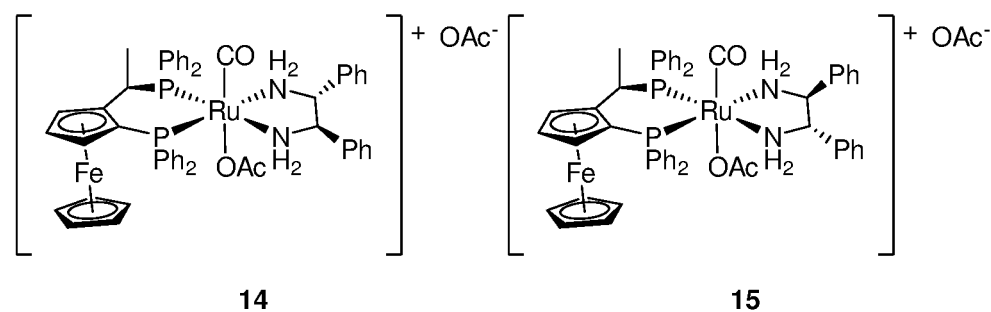
According to a further embodiment, the present disclosure may refer to a process to obtain complexes of formula (VII) with the limitations described above.

The synthetic route described above gives access to several diphosphine derivatives, including derivatives of achiral and chiral diphosphine ligands.

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



10



The cationic monocarbonyl derivatives **8** and **9** were obtained either from the polymer  $[\text{RuCl}_2(\text{CO})_2]_n$ , synthesized by reaction of  $\text{RuCl}_3 \cdot 2.5\text{H}_2\text{O}$  with formic acid or from the complex  $\text{RuCl}_2(\text{CO})(\text{dmf})(\text{PPh}_3)_2$ . Reaction of  $[\text{RuCl}_2(\text{CO})_2]_n$  with 1,4-bis(diphenylphosphino) butane and ethylenediamine in 2-propanol led to **8**, whereas  
 5 using 1,1'-bis(diphenylphosphino) ferrocene, in place of 1,4-bis(diphenylphosphino) butane, gave **9**. Reaction of  $\text{RuCl}_2(\text{CO})(\text{dmf})(\text{PPh}_3)_2$  takes place in  $\text{CH}_2\text{Cl}_2$  and affords the same products.

The cationic monocarbonyl derivatives **10-15** were obtained from the complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  as starting product. The complex **10** was obtained by a one-pot  
 10 reaction of  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  with the ligands 1,4-bis(diphenylphosphino)butane and ethylenediamine in  $\text{CH}_2\text{Cl}_2$ . The complex **11** was obtained, in a similar manner, by using 2-(aminomethyl)pyridine in place of ethylenediamine. The complexes **12** and **13** were obtained using the ligand 1,1'-bis(diphenylphosphino)ferrocene in place of 1,4-bis(diphenylphosphino)butane and the ligands ethylenediamine and 2-  
 15 (aminomethyl)pyridine, respectively.

Similarly the complexes **14** and **15** were obtained from the diphosphine (*R*)-1-[(*S<sub>P</sub>*)-2-(diphenylphosphino)ferrocenylethyl]diphenylphosphine and the ligands (1*R*,2*R*)-1,2-diphenylethylenediamine and (1*S*,2*S*)-1,2-diphenylethylenediamine.

The ligands of the type HCNN (IIa-b) have the ability to act both as bidentate (IIa-b) or  
 20 tridentate ligands of the type (IIc-d) when deprotonated.

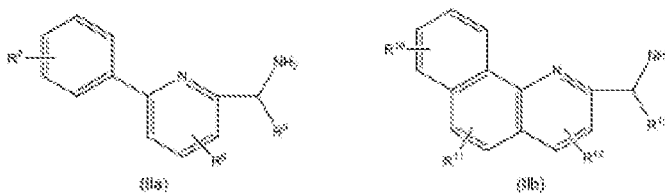
According to an embodiment, in the case of bidentate ligand the coordination occurs through the nitrogen atom of the  $-\text{NH}_2$  group and a second nitrogen atom of the heterocycle, in combination with a monophosphine to the metal. Thus, the present disclosure may refer to a complex of formula (VIII)



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

Preferably, the monodentate phosphine (P) is 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.

30 The present disclosure also refers to a process to obtain complexes of formula (VIII) comprising reacting a compound of formula  $\text{MXY}(\text{CO})(\text{PPh}_3)_2$ , or of formula  $\text{MXY}(\text{CO})(\text{PPh}_3)_2(\text{dmf})$ , wherein M, X, Y are as defined above and (dmf) is dimethylformamide, with a nitrogen-containing compound HCNN selected among:

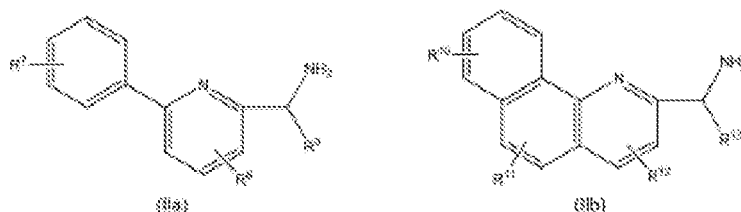


wherein

R<sup>7</sup> - R<sup>13</sup> are independently selected among H, C1-C20 aliphatic groups, and C5-C20 aromatic groups, preferably R<sup>8</sup>-R<sup>13</sup> may be H and/or R<sup>7</sup> may be 4-methyl, and optionally  
5 with a phosphine (P) selected among:

- a phosphine of formula PR<sup>16</sup>R<sup>17</sup>R<sup>18</sup>, wherein R<sup>16</sup> - R<sup>18</sup> are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; and
- an optically active phosphine selected among (*S*)-neomenthylidiphenylphosphine and (*R*)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl.

According to a preferred embodiment, the present disclosure may refer to a process to obtain a complex of formula (VIII) wherein M is Ru and X=Y= Cl or acetate (OAc) and P = PPh<sub>3</sub> by reacting RuCl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>(dmf) or Ru(OAc)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> with a nitrogen-containing compound HCNN selected among:

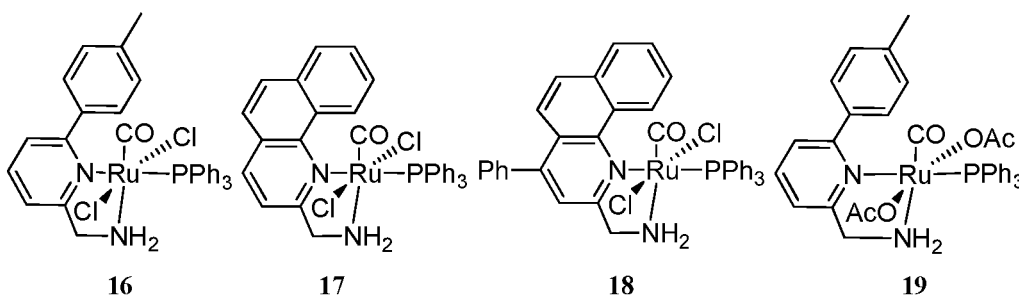


10

wherein

R<sup>7</sup> - R<sup>13</sup> are independently selected among H, C1-C20 aliphatic group and C5-C20 aromatic group, preferably R<sup>8</sup>-R<sup>13</sup> may be H and/or R<sup>7</sup> may be 4-methyl.

Examples of preferred complexes of formula (VIII) are:



The monocarbonyl phosphine derivatives **16-18** were isolated from RuCl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>(dmf) and 6-(4-methylphenyl)-2-(aminomethyl)pyridine, 2-

(aminomethyl)benzo[*h*]quinoline and 4-phenyl-2-(aminomethyl) benzo[*h*]quinoline in  $\text{CHCl}_3$ .

The neutral acetate monocarbonyl triphenylphosphine derivative **19** was obtained by reacting  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  and 6-(4-methylphenyl)-2-(aminomethyl)pyridine in toluene.

Known complexes such as  $\text{RuCl}_2(\text{CO})(\text{ampy})(\text{PPh}_3)$  (Cavarzan et al., *Polyhedron* 2013, 62, 75) shows remarkably lower activity and require a higher catalyst loading compared to compound **16** in transfer hydrogenation. The presence of the aromatic ring in the 6 position or the presence of a benzoquinoline ring lead to catalysts with a remarkably higher activity with respect to those containing the simple 2-(aminomethyl)pyridine ligand on account of the cyclometalation which occurs in the catalysis.

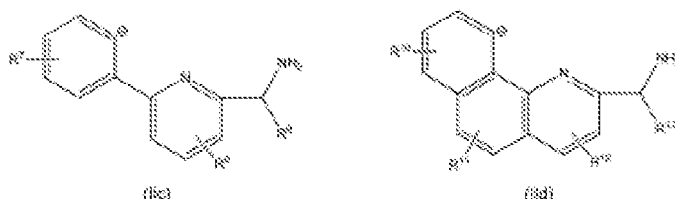
The HCNN ligands of the type (IIa), which contain a pyridine ring functionalized in the 6 position with an aromatic group, and those of the type (IIb), containing the benzo[*h*]quinoline system, have the ability to act as anionic tridentate ligands (IIc-d) through the nitrogen atom of the  $-\text{NH}_2$  group, a second nitrogen atom of the heterocycle and a cyclometalated carbon atom with the metal. Thus, according to a further embodiment, the present disclosure may refer to complexes of formula (IX)



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

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

- 5 (i) reacting a compound of formula  $\text{MXY}(\text{PPh}_3)_3$ , wherein M, X and Y are as described above, with a nitrogen-containing ligand (CNN) of formula (IIc) or (IId)



wherein

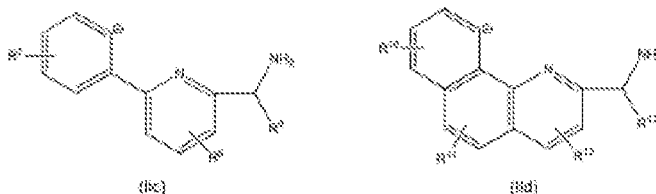
- 10  $\text{R}^7 - \text{R}^{13}$  are independently selected among H, C1-C20 aliphatic group and C5-C20 aromatic group, preferably  $\text{R}^8 - \text{R}^{13}$  may be H and/or  $\text{R}^7$  may be 4-methyl, and optionally a phosphine (P) selected among:

- 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*)-neomenthyl-diphenylphosphine and (*R*)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl, thereby obtaining an intermediate derivative and

(ii) reacting said derivative with CO.

- 5 According to a preferred embodiment, the present disclosure may refer to a process to obtain a complex of formula (IX) wherein M is Ru, X=Y= Cl and P=PPh<sub>3</sub> by reacting RuCl(CNN)(PPh<sub>3</sub>)<sub>2</sub> with CO where CNN is a nitrogen-containing ligand CNN selected among

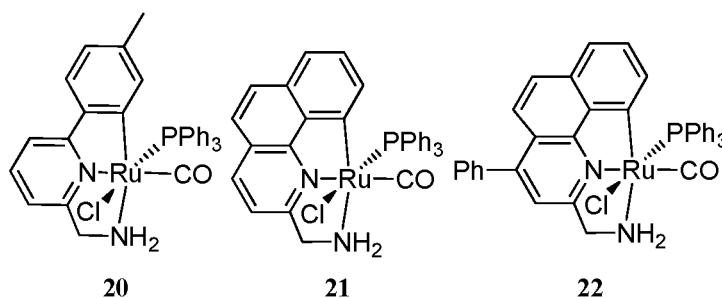


10 wherein

R<sup>7</sup> - R<sup>13</sup> are independently selected among H, C1-C20 aliphatic group and C5-C20 aromatic group, preferably R<sup>8</sup>-R<sup>13</sup> may be H and/or R<sup>7</sup> may be 4-methyl.

RuCl(CNN)(PPh<sub>3</sub>)<sub>2</sub> can be prepared according to processes known in the art, for example as described in WO2009/007443.

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



The monocarbonyl complexes **20-22** were obtained from the diphosphine pincer precursors RuCl(CNN)(PPh<sub>3</sub>)<sub>2</sub> (CNN = amtp, ambq and ambq<sup>Ph</sup>) by reaction with CO in CH<sub>2</sub>Cl<sub>2</sub>.

The anionic bidentate ligands of the type (IVb), obtained by deprotonation of an ortho-methyl group, have the ability through P and C atoms, in combination with a NN ligand, to coordinate ruthenium or osmium. Therefore, according to an embodiment, the present disclosure may refer to the complex of formula (X)

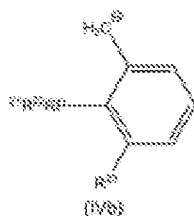


wherein M, X, (NN) and (CP) are as defined above, with the proviso that when X is Cl, (NN) is not ethylenediamine or 2-(aminomethyl)pyridine and (CP) is not a compound of formula (IVb) in which  $R^{21} = R^{22} = \text{phenyl}$  and  $R^{23} = \text{methyl}$ .

According to an embodiment,  $R^{23}$  may be  $-\text{CH}_3$  and/or  $R^{21} - R^{22}$  may be C6-C20 cycloaliphatic group or C6-C20 aromatic group, more preferably  $R^{23}$  may be  $-\text{CH}_3$  and/or  $R^{21} - R^{22}$  may be independently selected among phenyl and cyclohexyl group.

According to a further embodiment, the present disclosure may refer to a complex of formula (X) wherein M, X, (NN) and (CP) are as defined above, with the proviso that when X is Cl,  $R^{21}$  and  $R^{22}$  are not aromatic groups.

10 According to a further embodiment, the present disclosure may refer to a complex of formula (X) in which M, X, (NN) are as defined above, (CP) is a ligand of formula (IVb)

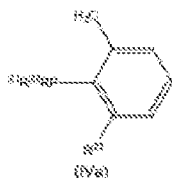


wherein

$R^{21} - R^{23}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably  $R^{23}$  may be  $-\text{CH}_3$  and/or  $R^{21} - R^{22}$  may be C6-C20 cycloaliphatic group or C6-C20 aromatic group, more preferably  $R^{23}$  may be  $-\text{CH}_3$  and/or  $R^{21} - R^{22}$  may be independently selected among phenyl and cyclohexyl group; with the proviso that when X is Cl,  $R^{21}$  and  $R^{22}$  are not aromatic groups.

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

(i) reacting  $\text{MX}_3 \cdot x\text{H}_2\text{O}$  with a HCP compound of formula (IVa)



wherein

M and X are as defined above and  $R^{21} - R^{23}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, thereby obtaining an intermediate complex of formula (XI); and

(ii) reacting the complex of formula (XI) with a (NN) ligand of formula Ia to Ic:

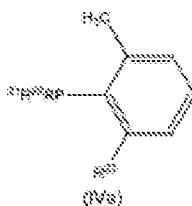


wherein

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

According to a preferred embodiment, the present disclosure may refer to a process to obtain a complex of formula (X) wherein M is Ru and X is Cl, comprising:

(i) reacting  $RuCl_3 \cdot xH_2O$  with a HCP compound of formula (IVa)

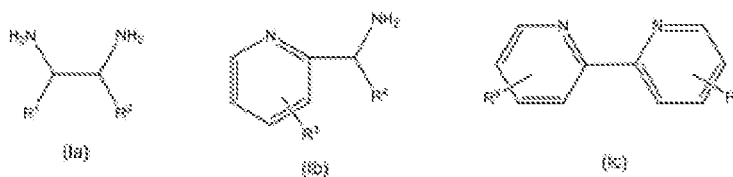


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wherein

$R^{21} - R^{23}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, thereby obtaining an intermediate complex of formula (XI); and

(ii) reacting the complex of formula (XI) with a (NN) ligand of formula (Ia-Ic):



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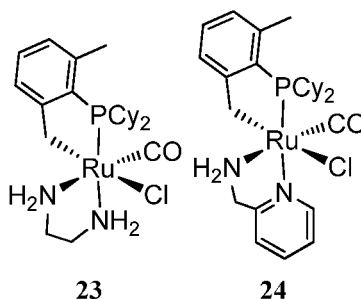
wherein

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

According to a further embodiment, the present disclosure may refer to a process to obtain complexes of formula (X) with the limitations described above.

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

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Complexes **23**, **24** were synthesized from **25** by reaction with ethylenediamine or 2-(aminomethyl)pyridine, respectively, via displacement of the phosphine.

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

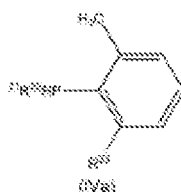


wherein M, X, (CP) and (HCP) are as defined above and with the proviso that when X is Cl and  $\text{R}^{23}$  is  $-\text{CH}_3$ ,  $\text{R}^{21}$  and  $\text{R}^{22}$  are not phenyl groups. According to an embodiment,  $\text{R}^{23}$  may be  $-\text{CH}_3$  and/or  $\text{R}^{21} - \text{R}^{22}$  may be C6-C20 cycloaliphatic group or C6-C20 aromatic group, preferably  $\text{R}^{21} - \text{R}^{22}$  may be cyclohexyl groups.

According to a specific embodiment, the present disclosure may refer to complexes of formula (XI) wherein M, X, (CP) and (HCP) are as defined above, with the proviso that when X is Cl,  $\text{R}^{21}$  and  $\text{R}^{22}$  are not an aromatic groups.

The complex of formula (XI) is a pentacoordinate complex.

The present disclosure also refers to a process to obtain complexes of formula (XI) comprising reacting  $\text{MX}_3 \cdot x\text{H}_2\text{O}$  with a HCP compound of formula (IVa)

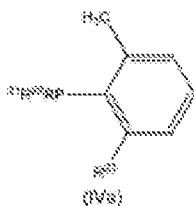


wherein

M and X are as defined above and  $\text{R}^{21} - \text{R}^{23}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups,  $\text{R}^{23}$  may be  $-\text{CH}_3$  and/or  $\text{R}^{21} - \text{R}^{22}$  may be C6-C20 cycloaliphatic group or C6-C20 aromatic group, preferably  $\text{R}^{21} - \text{R}^{22}$  may be cyclohexyl groups.

According to a preferred embodiment, the present disclosure may refer to a process to obtain complexes of formula (XI) in which M is Ru and X is Cl by reacting  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  with a HCP compound of formula (IVa)



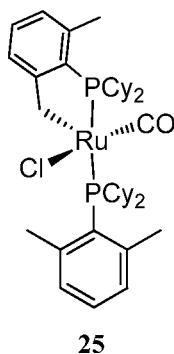


wherein

$R^{21}$  –  $R^{23}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups,  $R^{23}$  may be  $-\text{CH}_3$  and/or  $R^{21}$  -  $R^{22}$  may be C6-C20 cycloaliphatic group or C6-C20 aromatic group, preferably  $R^{21}$  -  $R^{22}$  may be cyclohexyl groups.

According to an embodiment, the present disclosure may refer to a process to prepare complexes of formula (XI) with the limitations described above.

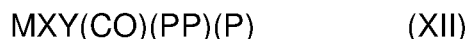
Non limiting examples of preferred complexes of formula (XI) is:



The complexes of formula (XI) may be synthesized using the anionic bidentate ligands of the type (IVb), obtained by deprotonation of an ortho-methyl group, which have the ability through P and C atoms, to coordinate ruthenium and osmium.

The cyclometallated monocarbonyl derivatives **25** was prepared by reaction of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  with (2,6-dimethylphenyl)dicyclohexylphosphine in ethanol and the presence of formaldehyde and triethylamine.

According to an embodiment, the present disclosure may refer to complexes of formula (XII)



wherein M, X, Y, (PP) and (P) are as defined above. Preferably, (P) is triphenylphosphine.

The present disclosure also refers to a process to obtain the complexes of formula (XII) comprising reacting a compound of formula  $\text{MXY}(\text{CO})(\text{PPh}_3)_2$ , or of formula  $\text{MXY}(\text{CO})(\text{PPh}_3)_2(\text{dmf})$ , wherein M, X, Y are as defined above and (dmf) is dimethylformamide, with a phosphine (P) selected among:

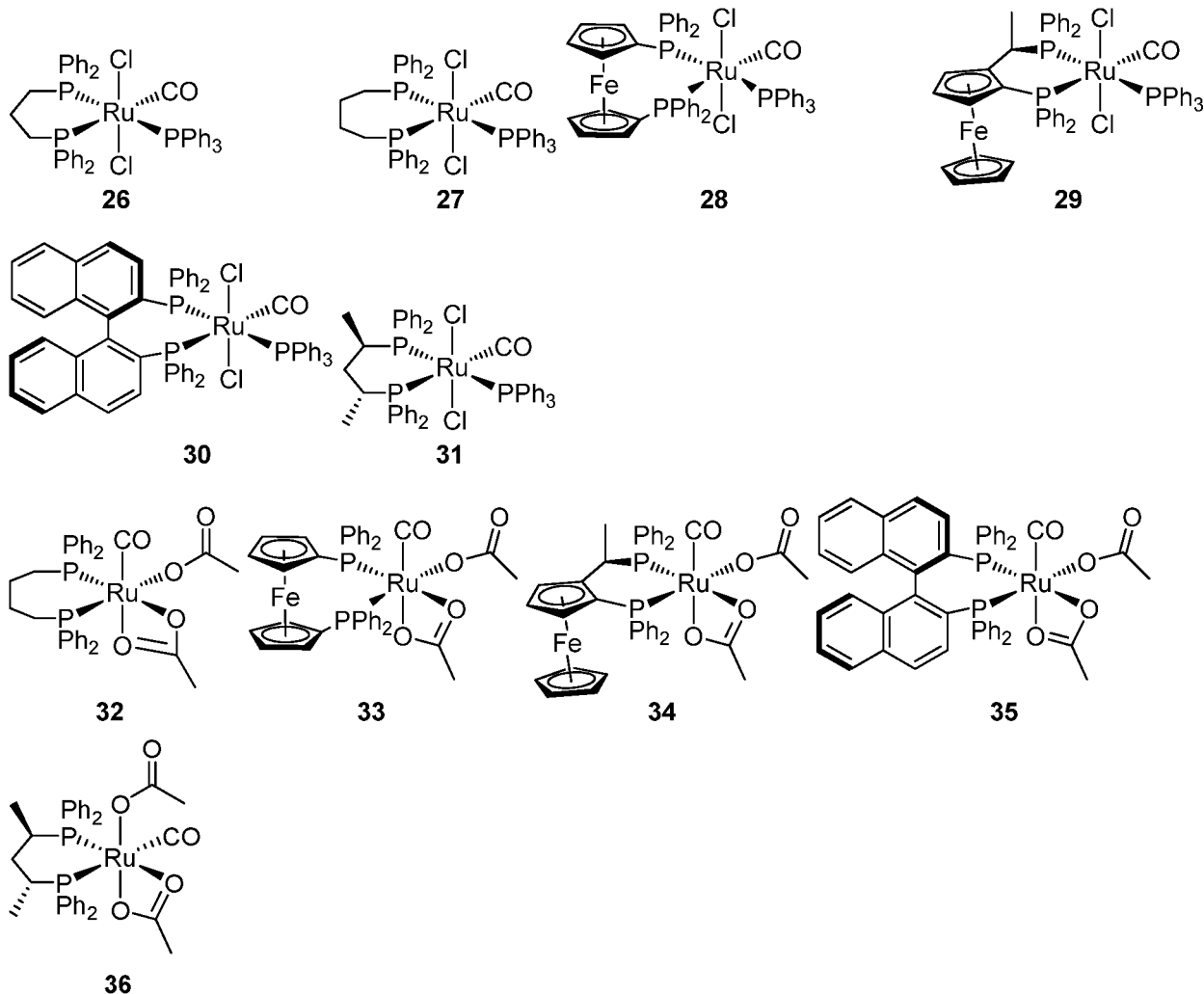
- a phosphine of formula  $PR^{16}R^{17}R^{18}$ , wherein  $R^{16} - R^{18}$  are independently selected among H, C1-C20 aliphatic group and C5-C20 aromatic groups;
  - an optically active phosphine selected among (*S*)-neomenthyldiphenylphosphine and (*R*)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl;
- 5 and a diphosphine (PP) selected among:
- a diphosphine of formula  $P(R^{19})_2 - Z - P(R^{20})_2$ , wherein Z is a C2-C4 aliphatic group 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;
- 10 - 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}ethyl dicyclohexyl phosphine, (*R*)-1-{2-[bis(3,5-dimethyl-4-
- 15 methoxyphenyl)phosphine]ferrocenyl}ethyl dicyclohexyl phosphine and (2*R*,4*R*)-2,4-bis(diphenylphosphine)pentane.

According to a preferred embodiment, the present disclosure refers to a process to obtain a complex of formula (XII) in which M is Ru and X is Cl or acetate group (OAc), by reacting  $RuCl_2(CO)(PPh_3)_2(dmf)$  or  $Ru(OAc)_2(CO)(PPh_3)_2$  with a phosphine (P) selected among:

- a phosphine of formula  $PR^{16}R^{17}R^{18}$ , wherein  $R^{16} - R^{18}$  are independently selected among H, C1-C20 aliphatic group and C5-C20 aromatic groups;
  - an optically active phosphine selected among (*S*)-neomenthyldiphenylphosphine and (*R*)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl;
- 20 and a diphosphine (PP) selected among:
- a diphosphine of formula  $P(R^{19})_2 - Z - P(R^{20})_2$ , wherein Z is a C2-C4 aliphatic group 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;
- 25 - 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}ethyl dicyclohexyl phosphine, (*R*)-1-{2-[bis(3,5-dimethyl-4-
- 30 phosphine,

methoxyphenyl)phosphine]ferrocenyl}ethyl)dicyclohexyl phosphine and (2*R*,4*R*)-2,4-bis(diphenylphosphine)pentane.

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



Complexes **26-36** have been synthesized by substitution of one or two triphenylphosphine from  $\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2(\text{dmf})$  or  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$ .

In a further embodiment, the present disclosure may refer to a complex of formula (XIII)



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

Preferably, the diphosphine (PP) is 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 aliphatic group or ferrocene optionally substituted with C1-C20 aliphatic groups, and wherein  $\text{R}^{19}$  and  $\text{R}^{20}$  are independently selected among C1-C20 aliphatic groups and C5-C20 aromatic groups.

The present disclosure also refers to a process to obtain a complex of formula (XIII) comprising reacting a compound of formula  $\text{MXY}(\text{CO})(\text{PPh}_3)_2$ , or of formula

MX<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>(dmf), wherein M, X, Y are as defined above and (dmf) is dimethylformamide, with a diphosphine (PP) selected among:

- a diphosphine of formula P(R<sup>19</sup>)<sub>2</sub>-Z-P(R<sup>20</sup>)<sub>2</sub>, wherein Z is a C2-C4 aliphatic group or ferrocene optionally substituted with C1-C20 aliphatic groups, and wherein R<sup>19</sup> and R<sup>20</sup>

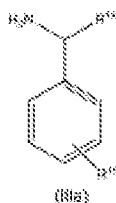
5 are independently selected among C1-C20 aliphatic groups and C5-C20 aromatic groups;

- 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),

10 dimethylmethyl)phosphine], (*R*)-1-{2-[diphenylphosphine]ferrocenyl}ethylcyclohexyl phosphine, (*R*)-1-{2-[bis(3,5-dimethyl-4-

methoxyphenyl)phosphine]ferrocenyl}ethylcyclohexyl phosphine and (*2R,4R*)-2,4-bis(diphenylphosphine)pentane;

and a nitrogen-containing ligand (HCN) of formula IIIa



15

wherein

R<sup>14</sup> and R<sup>15</sup> are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably R<sup>14</sup> and R<sup>15</sup> may be independently H.

According to a specific embodiment, the present disclosure refers to a process to obtain  
 20 a complex of formula (XIII) in which M is Ru and X is Cl or acetate group, by reacting a compound of formula RuCl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>(dmf) or Ru(OAc)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> with a phosphine (PP) selected among:

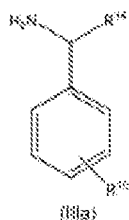
- a diphosphine of formula P(R<sup>19</sup>)<sub>2</sub>-Z-P(R<sup>20</sup>)<sub>2</sub>, wherein Z is a C2-C4 aliphatic group or ferrocene optionally substituted with C1-C20 aliphatic groups, and wherein R<sup>19</sup>

25 and R<sup>20</sup> 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),

30 dimethylmethyl)phosphine], (*R*)-1-{2-[bis(3,5-dimethyl-4-

[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; and a nitrogen-containing ligand (HCN) of formula IIIa

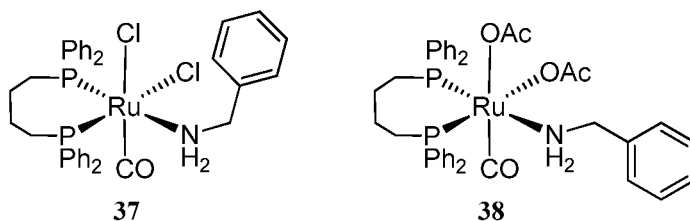


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wherein

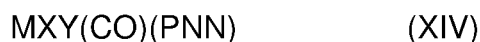
$R^1 - R^{15}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably  $R^{14}$  and  $R^{15}$  may be independently H.

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



In a further embodiment, the present disclosure may refer to a complex of formula (XIV)

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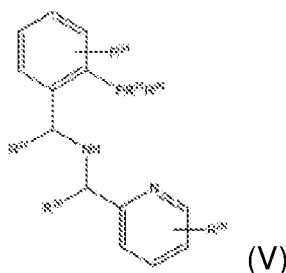


wherein M, X, Y and (PNN) are as defined above.

According to a specific embodiment, the present disclosure may refer to complexes of formula (XIV) wherein M, X, Y and (PNN) are as defined above, provided that when  $X = Y$ , X and Y are not Cl.

15

The present disclosure also refers to a method to obtain the complexes of formula (XIV) comprising reacting a compound of formula  $\text{MXY}(\text{CO})(\text{PPh}_3)_2$ , or of formula  $\text{MXY}(\text{CO})(\text{PPh}_3)_2(\text{dmf})$ , wherein M, X, Y are as defined above and (dmf) is dimethylformamide with a tridentate (PNN) ligand of formula (V)

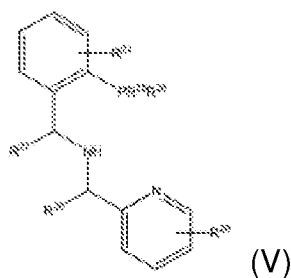


20

wherein

$R^{24} - R^{29}$  are independently selected among H, C1-C20 alkyl group and C5-C20 aryl groups, preferably  $R^{24}$  and  $R^{27}-R^{29}$  may be H and/or  $R^{25}$  and  $R^{26}$  may be a C1-C20 aromatic group, more preferably a phenyl group.

- 5 According to a specific embodiment, the present disclosure may refer to a process to obtain a complex of formula (XIV) in which M is Ru and X is acetate group comprising reacting a compound of formula  $Ru(OAc)_2(CO)(PPh_3)_2$  with a tridentate (PNN) ligand of formula (V)

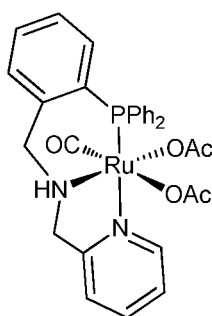


10 wherein

$R^{24} - R^{29}$  are independently selected among H, C1-C20 alkyl groups and C5-C20 aryl groups, preferably  $R^{24}$  and  $R^{27}-R^{29}$  may be H and/or  $R^{25}$  and  $R^{26}$  may be a C1-C20 aromatic group, more preferably a phenyl group.

- 15 According to a further embodiment, the present disclosure may refer to a process to obtain a complex of formula (XIV) with the limitations described above.

A non-limiting example of complexes of formula (XIV) is:



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- 20 Complexes of formula (1) and sub-formulas (VI-XIV) have been found to be highly active in transfer hydrogenation of ketones and aldehydes and can be used in hydrogenation of the same compounds using molecular hydrogen.

A further aspect of the present disclosure is the use of the complex of formula (1) or of sub-formulas (VI-XIV) 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 from the group consisting of C3-C42 ketones and C2-C41 aldehydes thereby obtaining a mixture; and
- (b) contacting said mixture with molecular H<sub>2</sub> or with at least one hydrogen-donor, preferably 2-propanol, sodium formate, ammonium formate, a mixture of formic acid and triethylamine,

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



wherein

M = Ru or Os;

a, b and d are independently 0 or 1;

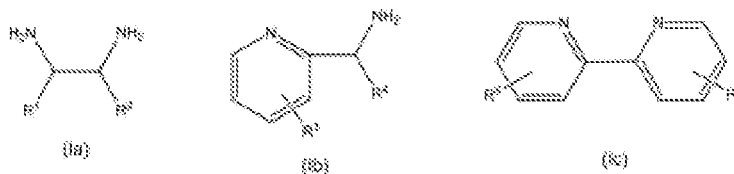
c is 1 or 2;

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

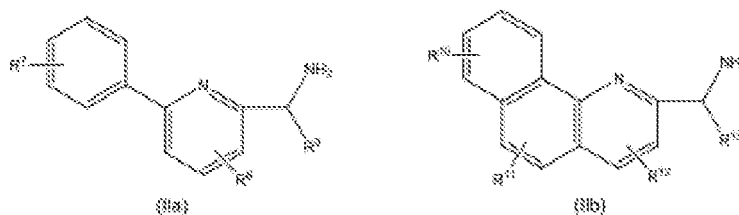
W is selected among halides, C1-C20 carboxylates and C1-C20 alkoxides;

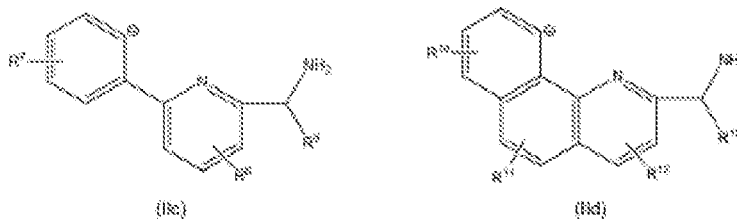
L is a nitrogen-containing ligand selected among:

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

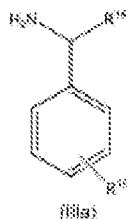


- (II) a HCNN compound of formula IIa – IIb and a CNN ligand of formula IIc – IId:





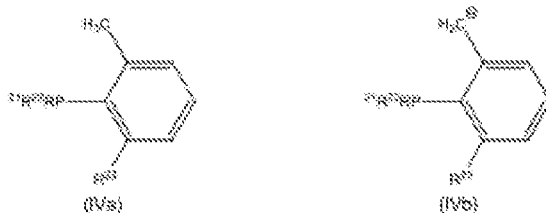
(III) a HCN compound of formula IIIa



wherein

- 5  $R^1 - R^{15}$  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  $R^8-R^{15}$  may be H and/or  $R^7$  may be 4-methyl;
- $L'$  is at least one phosphorus-containing ligand selected among:
- a phosphine (P) selected among: a phosphine of formula  $PR^{16}R^{17}R^{18}$ , wherein  $R^{16} - R^{18}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; an optically active phosphine selected among (*S*)-neomenthylidiphenylphosphine and (*R*)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl;
  - a diphosphine (PP) selected among: a diphosphine of formula  $P(R^{19})_2 - Z - P(R^{20})_2$ ,  
15 wherein Z is a C2-C4 aliphatic group 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),  
20 (*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 (2*R*,4*R*)-2,4-bis(diphenylphosphine)pentane;
  - a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



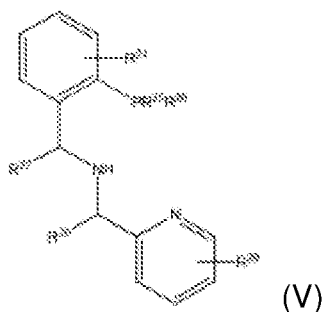


wherein

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

5 or C6-C20 aromatic group, preferably  $R^{21} - R^{22}$  may be cyclohexyl groups;

- a PNN compound of formula (V)



wherein

$R^{24} - R^{29}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably  $R^{24}$  and  $R^{27} - R^{29}$  may be H and/or  $R^{25}$  and  $R^{26}$  may be a C1-C20 aromatic group, more preferably a phenyl group.

According to a further embodiment, the present disclosure may refer to a process for the reduction of ketones or aldehydes to the corresponding alcohols, wherein the catalyst or pre-catalyst is a pentacoordinate or a hexacoordinate complex of general formula (1) with at least one of the limitations described above.

10 The complex of formula (1) containing only phosphorus-containing ligands  $L'$  is conveniently used as pre-catalyst in transfer hydrogenation or hydrogenation with molecular hydrogen, wherein the (transfer)hydrogenation is carried out in the presence of a nitrogen-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 the

15 following steps:

(a) mixing a pre-catalyst 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 thereby obtaining a mixture; and

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

wherein said pre-catalyst has general formula (2):



wherein

M = Ru or Os;

a, b and d are independently 0 or 1;

c is 1 or 2;

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

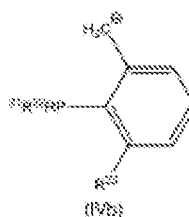
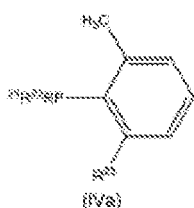
W is selected among halides, C1-C20 carboxylates and C1-C20 alkoxides;

L' is at least one phosphorus-containing ligand selected among:

- a phosphine (P) selected among: a phosphine of formula PR<sup>16</sup>R<sup>17</sup>R<sup>18</sup>, wherein R<sup>16</sup> -  
15 R<sup>18</sup> are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; an optically active phosphine selected among (S)-neomenthylidiphenylphosphine and (R)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl;

- a diphosphine (PP) selected among: a diphosphine of formula P(R<sup>19</sup>)<sub>2</sub> - Z - P(R<sup>20</sup>)<sub>2</sub>,  
20 wherein Z is a C2-C4 aliphatic group or ferrocene optionally substituted with C1-C20 aliphatic groups, and wherein R<sup>19</sup> and R<sup>20</sup> 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),  
25 (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;

- a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



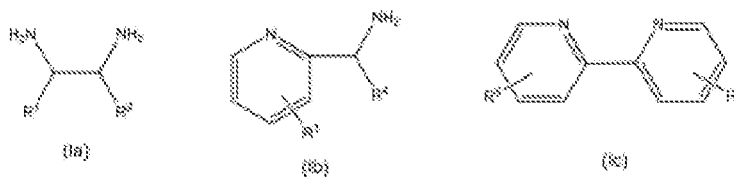
wherein

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

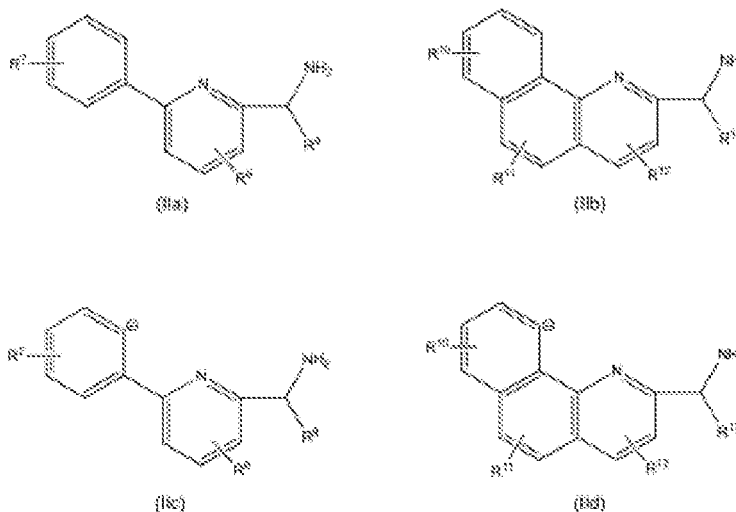
5 and wherein

step (a) is carried out by mixing said pre-catalyst with a solution further comprising at least one nitrogen-containing compound L selected among:

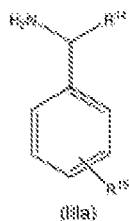
(i) a NN compound of formula Ia to Ic:



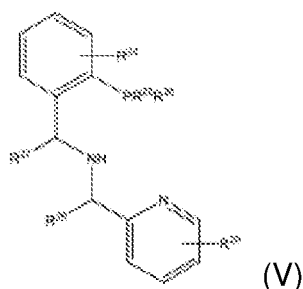
10 (ii) a HCNN compound of formula IIa – IIb and a CNN ligand of formula IIc – IId:



(iii) a HCN compound of formula IIIa



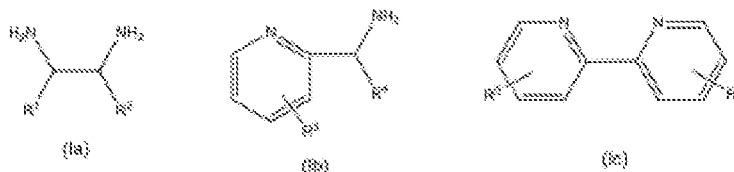
15 (iv) a PNN compound of formula (V)



wherein

$R^1 - R^{15}$  and  $R^{24} - R^{29}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, preferably  $R^1$  and  $R^2$  and  $R^{24} - R^{29}$  may be independently selected among H and a phenyl group and/or  $R^3 - R^6$  and  $R^8 - R^{15}$  may be H and/or  $R^7$  may be 4-methyl.

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



wherein  $R^1 - R^6$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups. More preferably, the nitrogen-containing compound is selected among ethylenediamine and 2-(aminomethyl)pyridine.

According to an embodiment, the step (a) of the processes described above may be conducted in the presence of a base, wherein said base may be potassium hydroxide, potassium carbonate or an alkali metal alkoxide preferably selected among sodium isopropoxide, potassium tert-butoxide, more preferably is potassium tert-butoxide, and in step (b) the mixture is contacted 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 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 good to complete.

The complex of the present disclosure can 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, the substrate may be:

- at least one C3-C41 ketone selected among compounds of formula  $R^{30}C(=O)R^{31}$  5 wherein  $R^{30}$  and  $R^{31}$  are independently selected among C1-C20 aliphatic, substituted aliphatic, aromatic, substituted aromatic and heteroaromatic groups wherein optionally  $R^{30}$  and  $R^{31}$  are linked to form a cycle;
- at least one C2-C41 aldehyde is selected among compounds of formula  $R^{32}C(=O)H$ , 10 wherein  $R^{32}$  is selected among C1-C40 aliphatic, substituted aliphatic, aromatic, substituted aromatic and heteroaromatic 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.

- 15 According to a further embodiment, in the process of the present disclosure the molar ratio substrate/base may range from 10/1 to 100/1.

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

- In a further embodiment, the present disclosure may refer to complexes of formula (1) and (2) and of sub-formulas (VI-XIV) as described above, wherein X and Y are equal. 20 More preferably, the present disclosure may refer to complexes of formula (1) and (2) and of sub-formulas (VI-XIV) as described above, wherein X and Y are equal and are selected among Cl and acetate group.

In a further embodiment, the present disclosure may refer to a complex of formula (1) and (2) and of sub-formula (VII) as described above, wherein W is chlorine.

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.

Example 1: Synthesis of the complex  $RuCl_2(CO)(en)(PCy_3)$  (1)

- 25 The complex  $RuCl_2(CO)(dmf)(PPh_3)_2$  (250 mg, 0.31 mmol, 1 equiv), suspended in 5 mL of dichloromethane, was reacted with  $PCy_3$  (176 mg, 0.63 mmol, 2 equiv). After stirring the mixture for 3 hours at room temperature, the ligand en (25  $\mu$ L, 0.37 mmol, 1.2 equiv) was added and the solution was stirred for 3 hours at room temperature. The volume

was reduced to about half and the complex was precipitated by adding 5 mL of pentane. The obtained solid was filtered, washed 2 times with 10 mL of ethyl ether and dried under reduced pressure. Yield: 149 mg (89%). Anal. Calcd (%) for  $C_{21}H_{41}Cl_2N_2OPRu$ : C, 46.66; H, 7.65; N, 5.18, Found: C, 46.39; H, 7.49; N, 5.36.  $^1H$  NMR (200 MHz,  $CD_2Cl_2$ )  $\delta$  3.77 – 3.62 (m, 2H), 3.35 – 3.20 (m, 2H), 3.09 (dd,  $J$  = 10.9, 5.5 Hz, 2H), 2.92 (dd,  $J$  = 9.7, 6.0 Hz, 2H), 2.32 – 1.08 (m, 33H).  $^{13}C$  NMR (50 MHz,  $CD_2Cl_2$ )  $\delta$  206.0 (d,  $J$  = 16.8 Hz), 43.5 (d,  $J$  = 2.8 Hz), 42.3 (d,  $J$  = 1.5 Hz), 35.3 (d,  $J$  = 21.0 Hz), 29.7, 28.2 (d,  $J$  = 10.0 Hz), 27.0.  $^{31}P$  NMR (81.0 MHz,  $CD_2Cl_2$ )  $\delta$  45.5. IR ( $cm^{-1}$ ): 1936.

Example 2: Synthesis of the complex  $RuCl_2(CO)(ampy)(PCy_3)$  (2)

The complex  $RuCl_2(CO)(dmf)(PPh_3)_2$  (300 mg, 0.38 mmol, 1 equiv), suspended in 5 mL of dichloromethane, was reacted with the ligand  $PCy_3$  (210 mg, 0.75 mmol, 2 equiv). After stirring the mixture for 3 hours at room temperature, the ligand ampy (47  $\mu$ L, 0.45 mmol, 1.2 equiv) was added. The solution was stirred for 3 hours at room temperature, the volume was reduced to about half and the complex was precipitated by adding 5 mL of pentane. The obtained solid was filtered, washed 2 times with 10 mL of ethyl ether and dried under reduced pressure. Yield: 187 mg (84%). Anal. Calcd (%) for  $C_{25}H_{41}Cl_2OPRu$ : C, 51.02; H, 7.02; N, 4.76, Found: C, 51.26; H, 7.22; N, 4.57.  $^1H$  NMR (200 MHz,  $CD_2Cl_2$ )  $\delta$  9.11 (d,  $J$  = 5.5 Hz, 1H), 7.88 – 7.62 (m, 1H), 7.55 – 7.28 (m, 1H), 7.28 – 7.10 (m, 1H), 4.70 (t,  $J$  = 5.9 Hz, 2H), 4.20 (t,  $J$  = 5.6 Hz, 2H), 2.33 (ddt,  $J$  = 23.4, 12.1, 2.8 Hz, 3H), 2.18 – 1.06 (m, 30H).  $^{13}C$  NMR (50 MHz,  $CD_2Cl_2$ )  $\delta$  207.5 (d,  $J$  = 17.8 Hz), 160.1, 152.55, 137.6, 124.4 (d,  $J$  = 2.2 Hz), 121.7 (d,  $J$  = 2.0 Hz), 50.6 (d,  $J$  = 2.3 Hz), 34.5 (d,  $J$  = 21.1 Hz), 29.5, 28.1 (d,  $J$  = 10.1 Hz), 27.0.  $^{31}P$  NMR (81.0 MHz,  $CD_2Cl_2$ )  $\delta$  45.9. IR ( $cm^{-1}$ ): 1941.

Example 3: Synthesis of the complex  $RuCl_2(CO)(en)(P^iPr_3)$  (3)

The complex  $RuCl_2(CO)(dmf)(PPh_3)_2$  (81.7 mg, 0.10 mmol, 1 equiv), suspended in 5 mL of distilled dichloromethane, was reacted with the ligand  $P^iPr_3$  (25  $\mu$ L, 0.13 mmol, 1.3 equiv). After stirring the mixture for 3 hours at room temperature, the ligand en (11  $\mu$ L, 0.16 mmol, 1.6 equiv) was added. The solution was stirred for 3 hours at room temperature. The volume was reduced to about half and the complex was precipitated by adding 5 mL of pentane. The obtained solid was filtered, washed 2 times with 10 mL of ethyl ether and dried at reduced pressure. Yield: 28 mg (66%). Anal. Calcd (%) for  $C_{12}H_{29}Cl_2N_2OPRu$ : C, 34.29; H, 6.95; N, 6.66, Found: C, 34.00; H, 7.20; N, 6.60.  $^1H$  NMR (200 MHz,  $CD_2Cl_2$ )  $\delta$  3.70 – 3.51 (m, 2H), 3.39 – 3.23 (m, 2H), 3.09 (dd,  $J$  = 11.2, 5.7 Hz, 2H), 3.01 – 2.85 (m, 2H), 2.63 – 2.39 (m, 3H), 1.33 (dd,  $J$  = 13.1, 7.3 Hz, 18H).

$^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  205.8 (d,  $J = 17.0$  Hz), 43.5 (d,  $J = 2.9$  Hz), 42.2 (d,  $J = 1.7$  Hz), 25.1 (d,  $J = 22.4$  Hz), 19.6 (d,  $J = 0.7$  Hz).  $^{31}\text{P}$  NMR (81.0 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  55.8. IR ( $\text{cm}^{-1}$ ): 1921.

**Example 4: Synthesis of the complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{en})(\text{PPh}_3)$  (**4** and **5**)**

5 The complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  (150 mg, 0.19 mmol, 1 equiv) suspended in  $\text{CH}_2\text{Cl}_2$  (2 mL) was reacted with the ligand en (16  $\mu\text{L}$ , 0.24 mmol, 1.2 equiv). After stirring the mixture for 2 h at room temperature, the volume was reduced to about half and the complex was precipitated by adding 10 mL of *n*-heptane. The obtained solid was filtered, washed 3 times with ethyl ether (3 mL), once with *n*-pentane (3 mL) and dried  
10 under reduced pressure. Yield: 64 mg (58%) as a mixture of *cis* and *trans* complexes **4** and **5**, in 2/3 ratio respectively. Anal. Calcd (%) for  $\text{C}_{25}\text{H}_{29}\text{N}_2\text{O}_5\text{PRu}$ : C, 52.72; H, 5.13; N, 4.92, Found: C, 52.90; H, 5.02; N, 5.14.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.92 – 7.20 (m, 21H), 7.06 – 6.84 (m, 0.4H), 5.28 – 5.13 (m, 0.4H), 5.04 – 4.85 (m, 2H), 4.01 – 3.78 (m, 2H), 3.23 – 3.04 (m, 0.4H), 2.88 – 2.75 (m, 0.4H), 2.75 – 2.57 (m, 2.8H), 2.54 – 2.37  
15 (m, 2.8H), 1.98 (s, 1.2H), 1.62 (s, 6H), 1.58 (s, 1.2H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  205.1 (d,  $J = 17.9$  Hz), 204.7 (d,  $J = 17.9$  Hz), 181.6, 180.4, 179.4, 134.4 (d,  $J = 1.3$  Hz), 134.0 (d,  $J = 10.4$  Hz), 133.8 (d,  $J = 10.5$  Hz), 133.5 (d,  $J = 1.3$  Hz), 133.2 (d,  $J = 1.0$  Hz), 130.3, 130.3, 128.8 (d,  $J = 3.8$  Hz), 128.6 (d,  $J = 3.7$  Hz), 46.8 (d,  $J = 3.1$  Hz), 44.5 (d,  $J = 2.4$  Hz), 44.0 (d,  $J = 1.9$  Hz), 43.4 (d,  $J = 4.1$  Hz), 25.3, 24.4, 24.3.  $^{31}\text{P}$  NMR  
20 (81.0 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  51.6, 47.3. IR ( $\text{cm}^{-1}$ ): 1934, 1924.

**Example 5: Synthesis of the complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{ampy})(\text{PPh}_3)$  (**6** and **7**)**

The complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  (150 mg, 0.19 mmol, 1 equiv) suspended in  $\text{CH}_2\text{Cl}_2$  (2 mL) was reacted with the ligand Ampy (25  $\mu\text{L}$ , 0.24 mmol, 1.2 equiv). After stirring the mixture for 2 h at room temperature, the volume was reduced to about half and the  
25 complex was precipitated by adding 10 mL of *n*-heptane. The obtained solid was filtered, washed 3 times with ethyl ether (3 mL), once with *n*-pentane (3 mL) and dried under reduced pressure. Yield: 77 mg (64%) as a mixture of **6** and **7** in a 2/3 ratio respectively. Anal. Calcd (%) for  $\text{C}_{29}\text{H}_{29}\text{N}_2\text{O}_5\text{PRu}$ : C, 56.40; H, 4.73; N, 4.54, Found: C, 56.75; H, 4.59; N, 4.23.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  9.49 – 9.42 (m, 0.7H), 9.10 –  
30 8.66 (m, 0.7H), 8.59 – 8.48 (m, 1H), 7.83 – 7.22 (m, 25H), 5.40 (t,  $J = 5.7$  Hz, 1.4H), 4.21 (t,  $J = 6.2$  Hz, 1.4), 4.08 (dd,  $J = 16.2, 5.0$  Hz, 1H), 3.87 (ddd,  $J = 15.7, 9.8, 5.8$  Hz, 1H), 2.08 (s, 2.1H), 2.01 (s, 2.1H), 1.43 (s, 3H), 1.33 (s, 3H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  205.8 (d,  $J = 17.7$  Hz), 205.5 (d,  $J = 18.9$  Hz), 182.1, 179.8, 177.8, 163.4, 161.3 (d,  $J = 1.8$  Hz), 154.7, 150.3, 138.5, 138.0, 134.2 (d,  $J = 10.5$  Hz), 134.1 (d,  $J =$

10.5 Hz), 133.4, 133.0, 132.5, 130.5 (d,  $J = 2.3$  Hz), 130.4 (d,  $J = 2.5$  Hz), 128.8 (d,  $J = 9.8$  Hz), 128.6 (d,  $J = 9.8$  Hz), 124.2 (d,  $J = 2.8$  Hz), 123.6 (d,  $J = 2.4$  Hz), 121.2 (d,  $J = 1.8$  Hz), 121.0 (d,  $J = 1.4$  Hz), 52.9 (d,  $J = 2.3$  Hz), 49.5 (d,  $J = 3.5$  Hz), 25.0, 24.3, 24.1.  $^{31}\text{P}$  NMR (81.0 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  53.8, 49.8. IR ( $\text{cm}^{-1}$ ): 1945, 1923.

5 **Example 6: Synthesis of the complex  $[\text{RuCl}(\text{CO})(\text{en})(\text{dppb})]\text{Cl}$  (8)**

The complex  $[\text{RuCl}_2(\text{CO})_2]_n$  (50 mg, 0.22 mmol, 1 equiv) suspended in 5 mL of distilled isopropanol, was reacted with the ligand dppb (94 mg, 0.22 mmol, 1 equiv). After stirring the mixture for 2 hours at 90 °C, the ligand en (15  $\mu\text{L}$ , 0.22 mmol, 1 equiv) was added and stirred for further 2 hours at 90 °C. The solution was evaporated *in vacuo*, and the  
10 solid was dissolved in  $\text{CHCl}_3$  (3 mL) and stirred for 3 hours at room temperature. The volume was reduced by half, the complex was precipitated by adding 5 mL of pentane. The obtained solid was filtered, washed 2 times with 10 mL of ethyl ether and dried at reduced pressure. Yield: 151 mg (98%). Anal. Calcd (%) for  $\text{C}_{32}\text{H}_{36}\text{ClN}_2\text{O}_2\text{P}_2\text{Ru}$ : C, 56.60; H, 5.34; N, 4.13, Found: C, 56.59; H, 5.39; N, 4.20.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$   
15 7.84 – 7.65 (m, 4H), 7.56 – 7.29 (m, 16H), 3.68 – 3.37 (m, 2H), 3.05 – 2.74 (m, 4H), 2.65 – 2.35 (m, 4H), 2.18 – 1.87 (m, 2H), 1.76 – 1.52 (m, 4H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  199.5 (t,  $J = 13.6$  Hz), 137.1 (t,  $J = 13.8$  Hz), 135.9 (t,  $J = 13.9$  Hz), 134.6 (t,  $J = 5.1$  Hz), 131.6 (d,  $J = 3.6$  Hz), 130.4, 129.3 (t,  $J = 4.6$  Hz), 129.0 (t,  $J = 5.0$  Hz), 45.9, 25.5 (t,  $J = 13.8$  Hz), 24.9 (t,  $J = 16.2$  Hz), 22.1.  $^{31}\text{P}$  NMR (81.0 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  37.4. IR  
20 ( $\text{cm}^{-1}$ ): 1969.

**Example 7: Synthesis of the complex  $[\text{RuCl}(\text{CO})(\text{en})(\text{dppf})]\text{Cl}$  (9)**

The complex  $\text{RuCl}_2(\text{CO})(\text{dmf})(\text{PPh}_3)_2$  (200 mg, 0.25 mmol, 1 equiv) dissolved in  $\text{CH}_2\text{Cl}_2$  (2 mL) was reacted with the ligand dppf (160 mg, 0.29 mmol, 1.2 equiv) at room temperature for 2 h. The ligand en (15  $\mu\text{L}$ , 0.37 mmol, 1.5 equiv) was then added and  
25 the mixture was stirred at room temperature for 2 h. The solution was concentrated to about 0.5 mL and the complex was precipitated by addition of *n*-heptane (10 mL). The obtained solid was filtered and thoroughly washed 4 times with ethyl ether (3 mL) and dried under reduced pressure. Yield: 180 mg (88%). Anal. Calcd (%) for  $\text{C}_{37}\text{H}_{36}\text{Cl}_2\text{FeN}_2\text{OP}_2\text{Ru}$ : C, 54.56; H, 4.46; N, 3.44, Found: C, 54.50; H, 4.51; N, 3.47.  $^1\text{H}$   
30 NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.97 – 7.24 (m, 20H), 5.59 (s, 2H), 5.15 – 4.91 (m, 2H), 4.53 (s, 2H), 4.20 (s, 2H), 3.97 (s, 2H), 3.68 – 3.42 (m, 2H), 2.58 – 2.41 (m, 2H), 2.14 – 1.85 (m, 2H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  204.0 (t,  $J = 14.8$  Hz), 135.9 (t,  $J = 5.7$  Hz), 134.2, 134.1 (d,  $J = 10.1$  Hz), 133.4, 132.9 (t,  $J = 4.7$  Hz), 132.0, 130.7, 130.4 (d,  $J =$



2.4 Hz), 129.2 – 128.3 (m), 77.8 (t,  $J = 4.9$  Hz), 75.7 (t,  $J = 3.2$  Hz), 73.5 (t,  $J = 3.3$  Hz), 71.3 (t,  $J = 3.0$  Hz), 45.7.  $^{31}\text{P}$  NMR (81.0 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  39.8. IR ( $\text{cm}^{-1}$ ): 1960.

**Example 8: Synthesis of the complex  $[\text{Ru}(\text{OAc})(\text{CO})(\text{en})(\text{dppb})]\text{OAc}$  (10)**

The complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  (200 mg, 0.26 mmol, 1 equiv) suspended in  $\text{CH}_2\text{Cl}_2$   
5 (2 mL) was reacted with the ligand dppb (120 mg, 0.29 mmol, 1.1 equiv) at room temperature for 6 h. The ligand en (25  $\mu\text{L}$ , 0.37 mmol, 1.4 equiv) was added and the solution was stirred at room temperature for further 2 h. The solution was concentrated to about 0.5 mL and the complex was precipitated by addition of *n*-heptane (10 mL). The obtained solid was filtered and washed 4 times with ethyl ether (3 mL) and dried  
10 under reduced pressure. Yield: 182 mg (97%). Anal. Calcd (%) for  $\text{C}_{35}\text{H}_{42}\text{N}_2\text{O}_5\text{P}_2\text{Ru}$ : C, 57.29; H, 5.77; N, 3.82 Found: C, 57.70; H, 5.90; N, 3.50.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.64 – 7.30 (m, 21H), 4.76 – 4.62 (m, 1H), 4.30 – 4.14 (m, 1H), 4.10 – 3.92 (m, 1H), 2.92 – 2.47 (m, 6H), 1.86 (s, 3H), 1.58 (s, 3H), 1.31 – 1.18 (m, 2H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  203.8 (t,  $J = 17.7$  Hz), 182.7, 182.5, 134.8 (d,  $J = 10.5$  Hz), 134.4 – 134.1  
15 (m), 133.8 – 133.6 (m), 132.3, 131.7, 131.2 (d,  $J = 2.3$  Hz), 130.1 (t,  $J = 4.8$  Hz), 129.8 (t,  $J = 4.8$  Hz), 129.4 (d,  $J = 9.7$  Hz), 46.6 (d,  $J = 10.6$  Hz), 44.7 (d,  $J = 11.0$  Hz), 30.1 (d,  $J = 6.7$  Hz), 29.6 (d,  $J = 14.2$  Hz), 25.5, 24.0, 23.5.  $^{31}\text{P}$  NMR (81.0 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  37.1. IR ( $\text{cm}^{-1}$ ): 1939.

**Example 9: Synthesis of the complex  $[\text{Ru}(\text{OAc})(\text{CO})(\text{ampy})(\text{dppb})]\text{OAc}$  (11)**

In an NMR tube the complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppb})$  (32) (31 mg, 0.05 mmol, 1 equiv) suspended in 0.6 mL of toluene- $d_8$ , was reacted with the ligand ampy (5  $\mu\text{L}$ , 0.05 mmol, 1 equiv). After stirring the mixture at room temperature for 30 min, the sample was characterized by NMR. The sample was then dried under low pressure. Yield: 31.3 mg (87%). Anal. Calcd (%) for  $\text{C}_{39}\text{H}_{42}\text{N}_2\text{O}_5\text{P}_2\text{Ru}$ : C, 59.92; H, 5.42; N, 3.58 Found: C,  
25 60.30; H, 5.60; N, 3.20.  $^1\text{H}$  NMR (200 MHz, toluene- $d_8$ )  $\delta$  8.19 – 7.94 (m, 4H), 7.61 – 6.80 (m, 17H), 6.68 – 6.55 (m, 1H), 6.47 (dd,  $J = 7.0, 5.1$  Hz, 1H), 6.33 – 6.06 (m, 1H), 4.20 (t,  $J = 17.4$  Hz, 1H), 3.20 (t,  $J = 12.0$  Hz, 1H), 3.07 – 2.86 (m, 1H), 2.66 – 2.42 (m, 1H), 2.03 (s, 3H), 1.93 (s, 3H), 1.84 – 1.56 (m, 3H), 1.48 – 1.12 (m, 5H).  $^{13}\text{C}$  NMR (50 MHz, toluene- $d_8$ )  $\delta$  203.3, 187.6, 177.0, 163.2, 159.8, 149.1 (d,  $J = 22.9$  Hz), 135.6,  
30 134.9 – 132.0 (m), 130.5 – 129.4 (m), 121.3 (d,  $J = 13.4$  Hz), 121.3, 120.8, 50.4, 30.7, 30.1, 29.9, 29.4, 25.8, 24.6 (d,  $J = 4.2$  Hz).  $^{31}\text{P}$  NMR (81.0 MHz, toluene- $d_8$ )  $\delta$  46.4 (d,  $J = 28.8$  Hz), 34.0 (d,  $J = 29.0$  Hz). IR ( $\text{cm}^{-1}$ ): 1944, 1608, 1586.

**Example 10: Synthesis of the complex  $[\text{Ru}(\text{OAc})(\text{CO})(\text{en})(\text{dppf})]\text{OAc}$  (12)**

In an NMR tube the complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppf})$  (**33**) (31.9 mg, 0.04 mmol, 1 equiv) suspended in 0.6 mL of toluene- $d_8$ , was reacted with the ligand en (3  $\mu\text{L}$ , 0.05 mmol, 1.1 equiv). After heating the mixture at 90 °C for 3 h, the sample was dried. The residue was dissolved in  $\text{CD}_2\text{Cl}_2$  and characterized by NMR. The sample was then dried under  
5 low pressure. Yield: 30.3 mg (88%). Anal. Calcd (%) for  $\text{C}_{41}\text{H}_{42}\text{FeN}_2\text{O}_5\text{P}_2\text{Ru}$ : C, 57.15; H, 4.91; N, 3.25 Found: C, 57.10; H, 4.50; N, 2.91.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.94 – 7.20 (m, 20H), 4.67 – 4.04 (m, 8H), 3.08 – 2.46 (m, 8H), 1.78 (s broad, 6H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  203.18 (t,  $J = 15.1$  Hz), 181.34 (s), 176.62 (dd,  $J = 12.1, 5.5$  Hz), 134.53 (t,  $J = 5.2$  Hz), 134.01 (t,  $J = 5.3$  Hz), 132.99 (dd,  $J = 16.2, 13.5$  Hz), 131.31 (s),  
10 129.15 (t,  $J = 4.9$  Hz), 128.57 (t,  $J = 4.9$  Hz), 79.63 (dd,  $J = 65.8, 9.6$  Hz), 75.90 (t,  $J = 4.2$  Hz), 75.53 (t,  $J = 4.5$  Hz), 73.09 (t,  $J = 3.1$  Hz), 72.80 (t,  $J = 3.1$  Hz), 45.70 (s), 26.06 (s).  $^{31}\text{P}$  NMR (81.0 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  40.1. IR ( $\text{cm}^{-1}$ ): 1963, 1617, 1569.

Example 11: Synthesis of the complex  $[\text{Ru}(\text{OAc})(\text{CO})(\text{ampy})(\text{dppf})]\text{OAc}$  (**13**)

In an NMR tube the complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppf})$  (**33**) (30.4 mg, 0.04 mmol, 1 equiv) suspended in 0.6 mL of toluene- $d_8$ , was reacted with the ligand ampy (4  $\mu\text{L}$ , 0.04 mmol,  
15 1 equiv). After stirring at room temperature for 2 h, the sample was characterized by NMR. The sample was then dried under low pressure. Yield: 30.1 mg (87%). Anal. Calcd (%) for  $\text{C}_{45}\text{H}_{42}\text{FeN}_2\text{O}_5\text{P}_2\text{Ru}$ : C, 59.41; H, 4.65; N, 3.08 Found: C, 59.10; H, 4.40; N, 2.70.  $^1\text{H}$  NMR (200 MHz, toluene- $d_8$ )  $\delta$  8.68 (t,  $J = 8.5$  Hz, 2H), 8.25 – 8.10 (m, 2H),  
20 7.99 (t,  $J = 8.1$  Hz, 2H), 7.75 (t,  $J = 8.5$  Hz, 2H), 7.40 – 7.24 (m, 2H), 7.16 – 6.83 (m, 15H), 6.64 – 6.43 (m, 3H), 6.15 – 5.92 (m, 1H), 5.80 (s, 1H), 4.71 (s, 1H), 4.21 (s, 1H), 3.91 (s, 1H), 3.72 (s, 1H), 3.48 (s, 1H), 2.54 (t,  $J = 14.6$  Hz, 1H), 2.41 – 2.25 (m, 1H), 1.84 (s, 3H), 1.66 (s, 3H).  $^{13}\text{C}$  NMR (50 MHz, toluene- $d_8$ )  $\delta$  210.1 (d,  $J = 17.6$  Hz), 178.3, 177.0 (d,  $J = 2.8$  Hz), 160.1 (d,  $J = 3.9$  Hz), 149.1, 136.0 (d,  $J = 11.8$  Hz), 135.5,  
25 134.5 (d,  $J = 10.7$  Hz), 133.2 (d,  $J = 9.9$  Hz), 130.9, 130.0 (d,  $J = 17.4$  Hz), 128.3, 127.3, 121.3 (d,  $J = 15.4$  Hz), 77.0 (d,  $J = 3.8$  Hz), 76.5 (d,  $J = 7.1$  Hz), 75.3 (d,  $J = 7.3$  Hz), 75.0 (d,  $J = 5.4$  Hz), 74.8, 71.3 (d,  $J = 5.3$  Hz), 71.1 (d,  $J = 3.5$  Hz), 70.3 (d,  $J = 5.8$  Hz), 50.4, 26.1, 24.6 (d,  $J = 5.8$  Hz).  $^{31}\text{P}$  NMR (81.0 MHz, toluene- $d_8$ )  $\delta$  51.2 (d,  $J = 29.1$  Hz), 40.5 (d,  $J = 29.1$  Hz). IR ( $\text{cm}^{-1}$ ): 1959, 1609, 1586.

30 Example 12: Synthesis of the complex  $[\text{Ru}(\text{OAc})(\text{CO})((R,R)\text{-dpen})(R\text{-Josiphos})]\text{OAc}$  (**14**)

In an NMR tube the complex  $\text{Ru}(\text{OAc})_2(\text{CO})(R\text{-Josiphos})$  (**34**) (32.0 mg, 0.04 mmol, 1 equiv) suspended in 0.6 mL of toluene- $d_8$ , was reacted with the ligand ( $R,R$ )-dpen (8.2 mg, 0.04 mmol, 1 equiv). After stirring at room temperature for 2 h, the sample was

characterized by NMR, showing that 2 isomers of the desired product were obtained in a 4/1 ratio. The sample was then dried under low pressure. Yield: 39.1 mg (97%). Anal. Calcd (%) for  $C_{55}H_{54}FeN_2O_5P_2Ru$ : C, 63.40; H, 5.22; N, 2.69; Found: C, 63.00; H, 5.40; N, 2.50.  $^{31}P$  NMR (81.0 MHz, toluene- $d_8$ )  $\delta$  60.4 (d,  $J = 35.8$  Hz, minor dia), 51.0 (d,  $J = 34.7$  Hz, major dia), 41.1 (d,  $J = 34.6$  Hz, major dia), 25.7 (d,  $J = 35.8$  Hz, minor dia). IR ( $cm^{-1}$ ): 1957, 1601, 1558

**Example 13: Synthesis of the complex  $[Ru(OAc)(CO)((S,S)\text{-dpen})(R\text{-Josiphos})]OAc$  (15)**

In an NMR tube the complex  $Ru(OAc)_2(CO)(R\text{-Josiphos})$  (**34**) (29.9 mg, 0.04 mmol, 1 equiv) suspended in 0.6 mL of toluene- $d_8$ , was reacted with the ligand ( $S,S$ )-dpen (8.0 mg, 0.04 mmol, 1 equiv). After stirring at room temperature for 2 h, the sample was characterized by NMR, showing that 2 isomers of the desired product was obtained in a 7/3 ratio. The sample was then dried under low pressure. Yield: 36.7 mg (98%). Anal. Calcd (%) for  $C_{55}H_{54}FeN_2O_5P_2Ru$ : C, 63.40; H, 5.22; N, 2.69; Found: C, 63.30; H, 5.50; N, 2.60.  $^{31}P$  NMR (81.0 MHz, toluene- $d_8$ )  $\delta$  53.8 (d,  $J = 36.0$  Hz, minor dia), 52.6 (d,  $J = 34.4$  Hz, major dia), 41.9 (d,  $J = 34.5$  Hz, major dia), 36.1 (d,  $J = 36.1$  Hz, minor dia). IR ( $cm^{-1}$ ): 1956, 1602, 1562.

**Example 14: Synthesis of the complex  $RuCl_2(CO)(Hamtp)(PPh_3)$  (16)**

The complex  $RuCl_2(CO)(dmf)(PPh_3)_2$  (282.3 mg, 0.35 mmol, 1 equiv), suspended in 15 mL of  $CHCl_3$ , was reacted with the ligand HCNN (70.9 mg, 0.36 mmol, 1.1 equiv). The suspension was stirred at 60 °C overnight and the volume was reduced to about 1 mL. The complex was precipitated by addition of 10 mL of *n*-pentane. 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: 160,3 mg (69%). Anal. Calcd (%) for  $C_{32}H_{29}Cl_2N_2OPRu$ : C, 58.19; H, 4.43; N, 4.24; found: C, 58.20, H, 4.40; N, 4.  $^1H$  NMR (200 MHz,  $CD_2Cl_2$ )  $\delta$  7.89 – 7.07 (m, 22H), 4.50 (t,  $J = 6.1$  Hz, 2H), 3.13 (t,  $J = 5.7$  Hz, 2H), 2.49 (s, 3H).  $^{13}C$  NMR (50 MHz,  $CD_2Cl_2$ )  $\delta$  200.7 (d,  $J = 21.5$  Hz), 165.5, 161.4, 140.4, 139.4, 137.1, 134.1 (d,  $J = 9.6$  Hz), 133.2, 132.3, 130.27, 130.2 (d,  $J = 2.4$  Hz), 129.3, 128.3 (d,  $J = 10.0$  Hz), 126.0 (d,  $J = 2.3$  Hz), 119.8 (d,  $J = 1.4$  Hz), 66.0, 50.3, 21.6 (d,  $J = 12.2$  Hz).  $^{31}P$  NMR (81 MHz,  $CD_2Cl_2$ )  $\delta$  54.5. IR ( $cm^{-1}$ ): 1947.

**Example 15: Synthesis of the complex  $RuCl_2(CO)(Hambq)(PPh_3)$  (17)**

The complex  $RuCl_2(CO)(dmf)(PPh_3)_2$  (365 mg, 0.46 mmol, 1 equiv), suspended in 5 mL of *n*-BuOH, was reacted with the ligand Hambq (208 mg, 1.03 mmol, 2.2 equiv). The suspension was stirred at 130 °C overnight, the solvent was evaporated under reduced

pressure and the residue was dissolved in 1 mL of  $\text{CHCl}_3$ . The solution was stirred for 1 hour at room temperature and the complex was precipitated by addition of 10 mL ethyl ether. The solution was filtered, and the solid was washed 2 times with 3 mL of ethyl ether, one time with 3 mL of *n*-pentane and dried under reduced pressure. Yield: 291 mg (95%). Anal. Calcd (%) for  $\text{C}_{33}\text{H}_{27}\text{Cl}_2\text{N}_2\text{OPRu}$ : C, 59.11; H, 4.06; N, 4.18, found: C, 59.20; H, 4.10; N, 4.26.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.12 – 6.87 (m, 23H), 4.36 – 4.14 (m, 1H), 4.01 – 3.83 (m, 1H), 3.54 – 3.28 (m, 1H), 2.68 – 2.24 (m, 1H).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  36.9. IR ( $\text{cm}^{-1}$ ): 1920.

**Example 16: Synthesis of the complex  $\text{RuCl}_2(\text{CO})(\text{Hambq}^{\text{Ph}})(\text{PPh}_3)$  (18)**

The complex  $\text{RuCl}_2(\text{CO})(\text{dmf})(\text{PPh}_3)_2$  (245 mg, 0.31 mmol, 1 equiv), suspended in 5 mL of *n*-BuOH, was reacted with the ligand  $\text{HCl}\cdot\text{Hambq}^{\text{Ph}}$  (159 mg, 0.50 mmol, 1.6 equiv) and the base *n*-Bu<sub>3</sub>N (0.5 mL, 2 mmol, 6.6 equiv). After stirring at 130 °C overnight, the solvent was evaporated under reduced pressure, the residue dissolved in 3 mL of  $\text{CHCl}_3$  and the base  $\text{K}_2\text{CO}_3$  (200 mg, 1.39 mmol, 4.5 equiv) was added. The mixture was stirred for 2 h at room temperature, the mixture was filtered. The volume was reduced to about 1 mL and the complex was precipitated by addition of 10 mL ethyl ether. The solution was filtered, and the solid was washed 2 times with 3 mL of ethyl ether, one time with 3 mL of *n*-pentane and dried under reduced pressure. Yield: 101 mg (46%). Anal. Calcd (%) for  $\text{C}_{39}\text{H}_{31}\text{Cl}_2\text{N}_2\text{OPRu}$ : C, 62.74; H, 4.18; N, 3.75, found: C, 62.66; H, 4.10; N, 3.92.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  9.21 – 9.13 (m, 1H), 7.95 – 7.10 (m, 26H), 4.77 – 4.54 (m, 1H), 4.26 – 4.00 (m, 1H), 3.84 – 3.63 (m, 1H), 3.19 – 2.98 (m, 1H).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  36.9. IR ( $\text{cm}^{-1}$ ): 1924.

**Example 17: Synthesis of the complex  $\text{Ru}(\text{OAc})_2(\text{Hamtp})(\text{CO})(\text{PPh}_3)$  (19)**

The complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  (100,3 mg, 0.13 mmol, 1 equiv), suspended in 5 mL of toluene, was reacted with the ligand Hamtp (26,7 mg, 0.13 mmol, 1 equiv). After stirring at 110 °C for 2 days, the solution was concentrated to  $V \sim 0.5$  mL, and the complex was precipitated by addition of 7 mL of *n*-pentane. The mixture was filtered and the solid was washed 2 times with 5 mL of *n*-Heptane, two times with 3 mL of  $\text{Et}_2\text{O}$  and dried under reduced pressure. Yield: 37,1 mg (40%). Anal. Calcd (%) for  $\text{C}_{36}\text{H}_{35}\text{N}_2\text{O}_5\text{PRu}$ : C, 61.10; H, 4.98; N, 3.96, found: C, 60.90; H, 5.30; N, 3.80.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.28 – 8.02 (m, 1H), 7.79 – 7.60 (m, 6H), 7.46 – 7.37 (m, 6H), 7.30 – 7.17 (m, 6H), 7.10 – 7.03 (m, 1H), 6.91 (d,  $J = 8.4$  Hz, 1H), 6.73 – 6.58 (m, 1H), 4.41 (dd,  $J = 16.6, 6.5$  Hz, 1H), 4.32 – 4.07 (m, 2H), 3.53 – 3.30 (m, 1H), 2.14 (s, 3H), 2.07 (s, 3H), 1.20 (s, 3H).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  54,4. IR ( $\text{cm}^{-1}$ ): 1914, 1597, 1572.

**Example 18: Synthesis of the complex  $RuCl(amp)(CO)(PPh_3)$  (20)**

The complex  $RuCl(CNN)(PPh_3)_2$  (251.9 mg, 0.29 mmol, 1 equiv) was suspended in 5 mL of  $CH_2Cl_2$  and the mixture was stirred under CO atmosphere (1 atm) overnight at room temperature. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography, eluent  $CH_2Cl_2/Et_2O$  (9/1 to 1/1). Yield: 173 mg (94%). Anal. Calcd (%) for  $C_{32}H_{28}ClN_2OPRu$ : C, 61.59; H, 4.52; N, 4.49. Found: C, 61.74; H, 4.85; N, 4.66. IR ( $cm^{-1}$ ): 1905.

**Example 19: Synthesis of the complex  $RuCl(ambq)(CO)(PPh_3)$  (21)**

The complex  $RuCl(ambq)(PPh_3)_2$  (226 mg, 0.26 mmol, 1 equiv) was suspended in 5 mL of  $CH_2Cl_2$ , and the mixture was stirred under CO atmosphere (1 atm) overnight at room temperature. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography, eluent  $CH_2Cl_2/Et_2O$  (9/1 to 1/1). Yield: 132 mg (80%). Anal. Calcd (%) for  $C_{33}H_{26}ClN_2OPRu$ : C, 62.51; H, 4.13; N, 4.42. Found: C, 62.55; H, 4.10; N, 4.37.  $^1H$  NMR (200 MHz,  $CD_2Cl_2$ )  $\delta$  8.06 – 7.80 (m, 2H), 7.51 – 6.92 (m, 20H), 4.53 (dd,  $J = 16.9, 6.7$  Hz, 1H), 4.13 – 3.96 (m, 1H), 3.85 – 3.60 (m, 1H), 2.76 (t,  $J = 8.7$  Hz, 1H).  $^{13}C$  NMR (50 MHz,  $CD_2Cl_2$ )  $\delta$  207.9 (d,  $J = 17.5$  Hz), 172.2 (d,  $J = 12.8$  Hz), 156.1, 150.7, 142.5, 139.8, 135.5, 134.1 (d,  $J = 19.2$  Hz), 133.4, 133.0 (d,  $J = 10.2$  Hz), 133.0 (s), 130.1 (d,  $J = 2.3$  Hz), 129.6, 128.3 (d,  $J = 9.8$  Hz), 125.5, 122.4, 119.8, 116.7, 51.5.  $^{31}P$  NMR (81 MHz,  $CD_2Cl_2$ )  $\delta$  58.4. IR ( $cm^{-1}$ ): 1922.

**Example 20: Synthesis of the complex  $RuCl(ambq^{Ph})(CO)(PPh_3)$  (22)**

The complex  $RuCl(ambq^{Ph})(PPh_3)_2$  (119.8 mg, 0.13 mmol, 1 equiv) was suspended in 5 mL of  $CH_2Cl_2$  and the mixture stirred under CO atmosphere (1 atm) at room temperature overnight. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography, eluent  $CH_2Cl_2/Et_2O$  (9/1 to 1/1). Yield: 76.6 mg (85%). Anal. Calcd (%) for  $C_{39}H_{30}ClN_2OPRu$ : C, 65.96; H, 4.26; N, 3.94. Found: C, 66.31; H, 3.33; N, 4.12.  $^1H$  NMR (200 MHz,  $CD_2Cl_2$ )  $\delta$  8.17 – 6.89 (m, 26H), 4.57 (dd,  $J = 16.9, 6.5$  Hz, 1H), 4.14 (dd,  $J = 17.4, 10.0$  Hz, 1H), 3.83 (dd,  $J = 17.0, 7.6$  Hz, 1H), 2.99 (dd,  $J = 9.1, 7.0$  Hz, 1H).  $^{13}C$  NMR (50 MHz,  $CD_2Cl_2$ )  $\delta$  208.0 (d,  $J = 17.4$  Hz, CO), 172.6 (d,  $J = 12.8$  Hz, Ru-C), 155.8, 150.9, 148.7, 142.7, 139.9, 138.0, 134.0 (d,  $J = 9.1$  Hz), 133.1, 132.9, 132.9, 130.0 (d,  $J = 2.4$  Hz), 129.9, 129.6, 129.1, 128.8, 128.3 (d,  $J = 9.8$  Hz), 123.6, 120.6, 119.6, 117.2, 51.5.  $^{31}P$  NMR (81 MHz,  $CD_2Cl_2$ )  $\delta$  58.8. IR ( $cm^{-1}$ ): 1920.

**Example 21: Synthesis of the complex  $RuCl[(2-CH_2-6-Me-C_6H_3)PCy_2](CO)(en)$  (**23**)**

In an NMR tube the complex  $RuCl[(2-CH_2-6-Me-C_6H_3)PCy_2](CO)[(2,6-Me_2C_6H_3)PCy_2]$  (**25**) (15.5 mg, 0.02 mmol, 1 equiv) was dissolved in 0.6 mL of  $CD_2Cl_2$ . The ligand en (3  $\mu$ L, 0.04 mmol, 2 equiv) was added. The solution was heated at 50 °C for two days. The  $^{31}P$  NMR analysis of the tube showed the displacement of one ligand  $PCy_2(Xylyl)$  and the formation of two isomers of the desired complex **23**.  $^{31}P$  NMR (81 MHz,  $CD_2Cl_2$ )  $\delta$  97.4 (s, 1%), 84.5 (s, 35%), 81.1 (s, 23 %), 53.1 (s, 5%,  $OPCy_2(Xylyl)$ ), -4.23 (s, 37%,  $PCy_2(Xylyl)$ ).

**Example 22: Synthesis of the complex  $RuCl[(2-CH_2-6-Me-C_6H_3)PCy_2](CO)(ampy)$  (**24**)**

In an NMR tube the complex  $RuCl[(2-CH_2-6-Me-C_6H_3)PCy_2](CO)[(2,6-Me_2C_6H_3)PCy_2]$  (**25**) (15.5 mg, 0.02 mmol, 1 equiv) was dissolved in 0.6 mL of  $CD_2Cl_2$ . The ligand en (3  $\mu$ L, 0.04 mmol, 2 equiv) was added. The solution was heated at 50 °C for two days with formation of complex **24**.

**Example 23: Synthesis of the complex  $RuCl[(2-CH_2-6-Me-C_6H_3)PCy_2](CO)[(2,6-Me_2C_6H_3)PCy_2]$  (**25**)**

The complex  $RuCl_3 \cdot xH_2O$  (109 mg, 0.43 mmol, 1 equiv), suspended in 4 mL of EtOH, was reacted with the ligand  $(2,6-Me_2C_6H_3)PCy_2$  (345 mg, 1.14 mmol, 2.7 equiv) and the base  $Et_3N$  (250  $\mu$ L, 1.84 mmol, 4.3 equiv). After stirring at 80 °C for 1 h, formaldehyde (300  $\mu$ L, 37% solution in water, 3.70 mmol, 8.6 equiv) was added and the mixture was stirred at 80 °C overnight. The volume was reduced to about half and the obtained precipitated was filtered. The solid was washed two times with 2 mL of EtOH, once with 2 mL of  $Et_2O$  and dried under reduced pressure. Yield: 107 mg (32%). Anal. Calcd (%) for  $C_{41}H_{61}ClOP_2Ru$ : C, 64.09; H, 8.00, Found: C, 63.99; H, 8.95.  $^1H$  NMR (200 MHz,  $CD_2Cl_2$ )  $\delta$  7.32 – 6.86 (m, 6H), 3.78 (d,  $J = 12.9$  Hz, 1H), 3.58 (dd,  $J = 15.0, 6.7$  Hz, 1H), 2.97 – 1.11 (m, 53H).  $^{13}C$  NMR (50 MHz,  $CD_2Cl_2$ )  $\delta$  201.6 (dd,  $J = 14.4, 12.1$  Hz), 163.7 (dd,  $J = 33.6, 4.2$  Hz), 140.8 (d,  $J = 1.4$  Hz), 133.8 (d,  $J = 3.0$  Hz), 131.3 (d,  $J = 1.4$  Hz), 130.9 (d,  $J = 1.7$  Hz), 130.5 (d,  $J = 2.5$  Hz), 130.1 (d,  $J = 2.1$  Hz), 129.8 (d,  $J = 0.9$  Hz), 129.5 (d,  $J = 2.4$  Hz), 129.1 (d,  $J = 1.1$  Hz), 128.9 (d,  $J = 1.3$  Hz), 127.7 (d,  $J = 5.5$  Hz), 126.0 (d,  $J = 14.4$  Hz), 41.7 (d,  $J = 19.2$  Hz), 40.6, 39.4 (d,  $J = 13.7$  Hz), 39.2 (d,  $J = 8.1$  Hz), 35.4 (d,  $J = 13.9$  Hz), 33.9 (d,  $J = 25.5$  Hz), 32.6 (d,  $J = 5.9$  Hz), 31.6 (d,  $J = 4.6$  Hz), 30.8 (d,  $J = 10.5$  Hz), 30.6 (d,  $J = 3.1$  Hz), 30.1 (d,  $J = 4.1$  Hz), 29.9, 29.6 (d,  $J = 4.0$  Hz), 29.3, 28.8 (d,  $J = 8.5$  Hz), 28.5 – 25.8 (m), 23.7 (d,  $J = 2.2$  Hz), 23.2 (t,  $J = 4.0$  Hz), 22.7.  $^{31}P$  NMR (81 MHz,  $CD_2Cl_2$ )  $\delta$  67.2 (d,  $J = 281.4$  Hz), 40.0 (d,  $J = 281.6$  Hz). IR ( $cm^{-1}$ ): 1903.

**Example 24: Synthesis of  $RuCl_2(CO)(dppb)(PPh_3)$  (27)**

The complex  $RuCl_2(CO)(dmf)(PPh_3)_2$  (100.9 mg, 0.13 mmol, 1 equiv) suspended in 5 mL of  $CHCl_3$ , was reacted with the ligand dppb (54.6 mg, 0.13 mmol, 1 equiv). After stirring at 60 °C overnight, the solution was concentrated to about 1 mL. The complex was precipitated by addition of 10 mL *n*-heptane. The obtained solid was filtered, washed 3 times with 4 mL of *n*-heptane, 3 times with 3 mL of ethyl ether and dried under reduced pressure. Yield: 112.4 mg (75%). Anal. Calcd (%) for  $C_{47}H_{43}Cl_2OP_3Ru$ : C, 63.52; H, 4.88 Found: C, 64.93; H, 5.99.  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  7.85 – 7.70 (m, 4H), 7.66 – 6.97 (m, 28H), 6.89 – 6.69 (m, 3H), 3.15 – 2.95 (m, 1H), 2.72 – 2.40 (m, 3H), 2.34 – 2.16 (m, 2H), 1.77 – 1.52 (m, 2H).  $^{31}P$  NMR (81 MHz,  $CD_2Cl_2$ )  $\delta$  27.5 (t,  $J = 25.8$  Hz, 1P), 16.4 – 14.8 (m, 2P). IR ( $cm^{-1}$ ): 1954.

**Example 25: Synthesis of  $RuCl_2(CO)(dppf)$  (28)**

The complex  $RuCl_2(CO)(dmf)(PPh_3)_2$  (199.3 mg, 0.25 mmol, 1 equiv) suspended in 5 mL of toluene, was reacted with the ligand dppf (141.3 mg, 0.25 mmol, 1 equiv). After stirring the mixture at 110 °C for 2 h, the obtained solution was concentrated to about 1 mL, 10 mL *n*-heptane were added and the suspension was stirred at room temperature for 1 h. The precipitate was filtered, the obtained solid was washed 3 times with 4 mL of *n*-heptane, 3 times with 3 mL of ethyl ether and dried under reduced pressure. Yield: 99.5 mg (39%). Anal. Calcd (%) for  $C_{35}H_{28}Cl_2FeOP_2Ru$ : C, 55.73; H, 3.74 Found: C, 55.41; H, 3.33.  $^{31}P$  NMR (81 MHz,  $CD_2Cl_2$ )  $\delta$  53.6 (d,  $J = 27.2$  Hz), 46.6 (d,  $J = 26.8$  Hz). IR ( $cm^{-1}$ ): 1979.

**Example 26: Synthesis of  $RuCl_2(CO)((R)\text{-Josiphos})(PPh_3)$  (29)**

The complex  $RuCl_2(CO)(dmf)(PPh_3)_2$  (300.0 mg, 0.38 mmol, 1 equiv) suspended in 5 mL of toluene, was reacted with the ligand (*R*)-Josiphos (225.2 mg, 0.39 mmol, 1 equiv). After stirring the mixture at 110 °C 2 h, the obtained solution was concentrated to about 1 mL. The complex was precipitated by addition of 10 mL *n*-heptane, filtered, washed 3 times with 4 mL of *n*-heptane, 3 times with 3 mL of ethyl ether and dried under reduced pressure. Yield: 345.8 mg. Anal. Calcd (%) for  $C_{55}H_{47}Cl_2FeOP_3Ru$ : C, 63.23; H, 4.53; Found: C, 62.90; H, 4.20.  $^{31}P$  NMR (81 MHz,  $CD_2Cl_2$ )  $\delta$  47.5 (t,  $J = 22.9$  Hz), 13.6 (d,  $J = 22.7$  Hz). IR ( $cm^{-1}$ ): 1979.

**Example 27: Synthesis of  $RuCl_2(CO)((R)\text{-BINAP})(PPh_3)$  (30)**

The complex  $RuCl_2(CO)(dmf)(PPh_3)_2$  (299.7 mg, 0.38 mmol, 1 equiv) suspended in 5 mL of toluene, was reacted with the ligand (*R*)-BINAP (239.8 mg, 0.39 mmol, 1 equiv).

After stirring at 110 °C 2 h, the obtained solution was concentrated to about 1 mL. The complex was precipitated by addition of 10 mL *n*-heptane, filtered, washed 3 times with 4 mL of *n*-heptane, 3 times with 3 mL of ethyl ether and dried under reduced pressure. Yield: 359.7 mg (87%). Anal. Calcd (%) for C<sub>63</sub>H<sub>48</sub>Cl<sub>2</sub>OP<sub>3</sub>Ru: C, 69.68; H, 4.37; Found: C, 69.80; H, 4.10. IR (cm<sup>-1</sup>): 1981

**Example 28: Synthesis of RuCl<sub>2</sub>(CO)((*R,R*)-Skewphos)(PPh<sub>3</sub>) (31)**

The complex RuCl<sub>2</sub>(CO)(dmf)(PPh<sub>3</sub>)<sub>2</sub> (201.1 mg, 0.26 mmol, 1 equiv) suspended in 5 mL of toluene, was reacted with the ligand (*R,R*)-Skewphos (113.0 mg, 0.26 mmol, 1 equiv). After stirring at 110 °C 2 h, the solution was concentrated to about 1 mL. The complex was precipitated by addition of 10 mL *n*-heptane, filtered, washed 3 times with 4 mL of *n*-heptane, 3 times with 3 mL of ethyl ether and dried under reduced pressure. Yield: 150.5 mg (65%). IR (cm<sup>-1</sup>): 1976.

**Example 29: Synthesis of Ru(OAc)<sub>2</sub>(CO)(dppb) (32)**

The complex Ru(OAc)<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> (300.3 mg, 0.39 mmol, 1 equiv) suspended in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, was reacted with the ligand dppb (167.3 mg, 0.39 mmol, 1 equiv). After stirring the mixture at room temperature overnight, the obtained solution was concentrated to about 0.5 mL. The complex was precipitated by addition of 10 mL *n*-heptane, filtered, washed 3 times with 4 mL of *n*-heptane, 3 times with 3 mL of ethyl ether and dried under reduced pressure. Yield: 230.1 mg (88%). Anal. Calcd (%) for C<sub>33</sub>H<sub>34</sub>O<sub>5</sub>P<sub>2</sub>Ru: C, 58.84; H, 5.09 Found: C, 58.50; H, 5.10. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C) δ 7.92 – 7.12 (m, 20H), 2.84 (m, 2H), 2.43 (m, 2H), 1.79 (m, 4H), 1.41 (s, 6H). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, -70 °C) δ 8.07 – 7.77 (m, 3H), 7.73 – 7.19 (m, 15H), 7.15 – 6.92 (m, 2H), 3.37 – 2.36 (m, 3H), 2.29 – 1.38 (m, 5H), 1.34 (s, 3H), 1.14 (s, 3H). <sup>13</sup>C NMR (50 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) δ 204.6 (broad), 133.77 – 132.48 (m), 130.80 (d, *J* = 25.6 Hz), 129.07 – 128.33 (m), 30.40 (s, broad), 29.75 (s, broad), 23.79 (s, broad), 23.53 (s, broad). <sup>13</sup>C NMR (50 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -70 °C) δ 204.5 (dd, *J* = 21.6, 15.8 Hz), 202.7 (t, *J* = 16.9 Hz), 189.1, 182.4 (t, *J* = 38.8 Hz), 175.3, 136.8 (d, *J* = 51.5 Hz), 133.4 (d, *J* = 18.8 Hz), 131.8, 131.2 – 130.5 (m), 130.4 (d, *J* = 8.7 Hz), 129.4 (d, *J* = 17.3 Hz), 129.1 – 128.5 (m), 128.0 (d, *J* = 8.9 Hz), 127.8 (d, *J* = 9.5 Hz) 29.9 (d, *J* = 35.3 Hz), 27.7 (d, *J* = 33.5 Hz), 25.2, 24.4, 21.9 (d, *J* = 4.3 Hz), 20.5. <sup>31</sup>P NMR (81 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) δ 46.7 (broad). <sup>31</sup>P NMR (81 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -70 °C) δ 48.0 (d, *J* = 27.1 Hz), 46.3 (d, *J* = 25.9 Hz), 38.7 (s, broad). IR (cm<sup>-1</sup>): 1954, 1945.

**Example 30: Synthesis of Ru(OAc)<sub>2</sub>(CO)(dppe) (33)**



The complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  (200.5 mg, 0.26 mmol, 1 equiv) suspended in 5 mL of toluene, was reacted with the ligand dppf (167.3 mg, 0.26 mmol, 1 equiv). After stirring at 110 °C for 2 h, the solution was concentrated to about 1 mL and the complex was precipitated by addition of 10 mL *n*-heptane, filtered, washed 3 times with 4 mL of *n*-heptane, 3 times with 3 mL of ethyl ether and dried under reduced pressure. Yield: 139.6 mg (67%) determined to be a mixture of 3 isomers in a ratio of 7/2/1 at -70 °C, the mixture is interchanging at room temperature. Anal. Calcd (%) for  $\text{C}_{39}\text{H}_{34}\text{FeO}_5\text{P}_2\text{Ru}$ : C, 58.44; H, 4.28; Found: C, 58.10; H, 4.60.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  7.95 – 7.14 (m broad, 20 H), 4.68 – 4.24 (m broad, 8H), 1.56 (s broad, 6H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  134.9 – 133.1 (m), 130.7 (d,  $J = 16.0$  Hz), 129.1 – 127.2 (m), 75.5 (d,  $J = 36.2$  Hz), 73.1, 72.6, 24.2 (s, broad).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_2\text{Cl}_2$ , -70 °C)  $\delta$  203.07 (t,  $J = 16.5$  Hz), 182.69 (s), 181.93 (s), 134.64 (dd,  $J = 22.9, 9.9$  Hz), 132.95 (d,  $J = 9.7$  Hz), 132.24 – 130.81 (m), 129.84 (s), 127.92 – 126.43 (m), 78.20 – 76.66 (m), 75.95 (d,  $J = 5.4$  Hz), 75.53 – 74.02 (m), 72.71 (s), 71.80 (d,  $J = 6.1$  Hz), 71.14 (d,  $J = 5.4$  Hz), 25.40 (s), 24.47 (d,  $J = 4.8$  Hz).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  50.8 (s broad).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ , -70 °C)  $\delta$  53.1 (d,  $J = 27.1$  Hz, 10%), 52.0 (d,  $J = 26.7$  Hz, 23%), 49.8 (d,  $J = 30.4$  Hz), 45.4 (d,  $J = 30.4$  Hz, 67%), 43.5 (d,  $J = 26.8$  Hz, 10%). IR ( $\text{cm}^{-1}$ ): 1974, 1613.

**Example 31: Synthesis of  $\text{Ru}(\text{OAc})_2(\text{CO})((R)\text{-Josiphos})$  (34)**

The complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  (300.3 mg, 0.39 mmol, 1 equiv) suspended in 5 mL of toluene, was reacted with the ligand (*R*)-Josiphos (167.3 mg, 0.40 mmol, 1 equiv). After stirring at 110 °C for 2 h, the homogenous solution, was concentrated to about 1 mL and the complex was precipitated by addition of 10 mL *n*-heptane, filtered, washed 3 times with 4 mL of *n*-heptane, 3 times with 3 mL of ethyl ether and dried under reduced pressure, leading to a mixture of two diastereoisomers of the product in a 3/2 ratio. Yield: 273.6 mg (85%). Anal. Calcd (%) for  $\text{C}_{41}\text{H}_{38}\text{FeO}_5\text{P}_2\text{Ru}$ : C, 59.36; H, 4.62 Found: C, 59.30; H, 4.30.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  8.25 – 7.99 (m, 3H), 7.70 – 7.07 (m, 31H), 7.05 – 6.87 (m, 2H), 6.72 – 6.46 (m, 2H), 4.81 (s, 1H, maj dia), 4.65 (s, 1H min dia), 4.49 (s, 1H), 4.44 – 4.32 (m, 2H), 4.24 – 4.00 (m, 2H), 3.91 (s, 3H min dia), 3.76 (s, 5H maj dia), 2.09 – 1.65 (m, 4H), 1.51 – 1.25 (m, 8H).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  67.2 (broad, maj dia), 46.5 (broad, maj dia), 35.9 (broad, min dia), 30.5 (broad, min dia). IR ( $\text{cm}^{-1}$ ): 1975, 1950, 1614, 1568.

**Example 32: Synthesis of  $\text{Ru}(\text{OAc})_2(\text{CO})((R)\text{-BINAP})$  (35)**

The complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  (300.7 mg, 0.39 mmol, 1 equiv) suspended in 5 mL of toluene, was reacted with the ligand (*R*)-BINAP (243 mg, 0.39 mmol, 1 equiv). After stirring at 110 °C for 2 h, the solution was concentrated to about 1 mL. The complex was precipitated by addition of 10 mL *n*-heptane, filtered, washed 3 times with 4 mL of *n*-heptane, 3 times with 3 mL of ethyl ether and dried under reduced pressure. Yield: 314.1 mg (93%). Anal. Calcd (%) for  $\text{C}_{49}\text{H}_{38}\text{O}_5\text{P}_2\text{Ru}$ : C, 67.66; H, 4.40 Found: C, 68.00; H, 4.30.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  7.97 – 7.81 (m, 2H), 7.71 – 7.27 (m, 20H), 7.24 – 6.99 (m, 4H), 6.92 – 6.52 (m, 6H), 1.29 (s, 6H).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  49.87 (s broad), 43.21 (s broad). IR ( $\text{cm}^{-1}$ ): 1968, 1616, 1505.

10 **Example 33: Synthesis of  $\text{Ru}(\text{OAc})_2(\text{CO})((R,R)\text{-Skewphos})$  (36)**

The complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  (200.9 mg, 0.26 mmol, 1 equiv) suspended in 5 mL of toluene, was reacted with the ligand (*R,R*)-Skewphos (114 mg, 0.26 mmol, 1 equiv). After stirring at 110 °C for 2 h, the solution was concentrated to about 1 mL and the complex was precipitated by addition of 10 mL *n*-heptane, filtered, washed 3 times with 4 mL of *n*-heptane, 3 times with 3 mL of  $\text{Et}_2\text{O}$  and dried under reduced pressure. Yield: 127.9 mg (71%). Anal. Calcd (%) for  $\text{C}_{34}\text{H}_{36}\text{O}_5\text{P}_2\text{Ru}$ : C, 59.38; H, 5.28 Found: C, 59.20; H, 4.90; N, 4.10.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  7.78 – 7.34 (m, 16H), 7.32 – 7.08 (m, 4H), 3.28 – 3.03 (m, 1H), 2.85 – 2.64 (m, 1H), 2.26 – 2.06 (m, 1H), 2.00 – 1.77 (m, 1H), 1.57 (s broad, 6H), 0.95 (ddd,  $J = 19.4, 14.0, 7.1$  Hz, 6H).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  55.0 (s, broad), 50.9 (s, broad). IR ( $\text{cm}^{-1}$ ): 1958, 1568.

20 **Example 34: Synthesis of  $\text{RuCl}_2(\text{CO})(\text{dppb})(\text{HCN})$  (37)**

The complex  $\text{RuCl}_2(\text{CO})(\text{dmf})(\text{PPh}_3)_2$  (159.1 mg, 0.20 mmol, 1 equiv) suspended in 3 mL of  $\text{CH}_2\text{Cl}_2$ , was reacted with the ligand dppb (85.3 mg, 0.20 mmol, 1 equiv) and stirred at room temperature for 2 h. The solution was dried under vacuum and 2-propanol (3 ml) and the ligand HCN (0.3 mmol, 33  $\mu\text{l}$ , 1.5 eq.) were sequentially added to the obtained residue and the mixture refluxed for 2.5 h. The solvent was evaporated under reduced pressure and the crude product was treated with *n*-pentane and refluxed for 0.5 h. The precipitated complex was filtrated, washed 3 times with 4 mL of pentane and dried under reduced pressure. Yield: 92 mg (63%).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  47.6 (d,  $J = 30.2$  Hz), 28.2 (d,  $J = 30.2$  Hz).

30 **Example 35: Synthesis of  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppb})(\text{HCN})$  (38)**

The complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  (154.3 mg, 0.20 mmol, 1 equiv) suspended in 3 mL of  $\text{CH}_2\text{Cl}_2$ , was reacted with the ligand dppb (85.3 mg, 0.20 mmol, 1 equiv) and stirred at room temperature for 2 h. The solvent was evaporated under reduced pressure and

2-propanol (3 ml) and the ligand HCN (0.3 mmol, 33  $\mu$ l, 1.5 eq.) were sequentially added and the mixture was refluxed for 2.5 h. The solvent was evaporated under reduced pressure and the crude product was treated with pentane and refluxed for 0.5 h (3 x 3 ml). The precipitated complex was filtrated and dried under reduced pressure.

5 Yield: 90 mg (58%).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ , 25  $^\circ\text{C}$ )  $\delta$  45.1 (d,  $J = 29.1$  Hz), 34.7 (d,  $J = 29.1$  Hz).

Example 36: Synthesis of  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PNN})$  (39)

The complex  $\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)_2$  (201.2 mg, 0.26 mmol, 1 equiv) suspended in 5 mL of toluene, was reacted with the ligand PNN (101.4 mg, 0.27 mmol, 1 equiv). After  
10 stirring at 110  $^\circ\text{C}$  for 2 h, the solution was concentrated to about 1 mL. The complex was precipitate by addition of 10 mL *n*-heptane, filtrated, washed 3 times with 4 mL of *n*-heptane, 3 times with 3 mL of ethyl ether and dried under reduced pressure. Yield: 142.1 mg (87%). Anal. Calcd (%) for  $\text{C}_{30}\text{H}_{29}\text{N}_2\text{O}_5\text{PRu}$ : C, 57.23; H, 4.64; N, 4.45 Found: C, 57.60; H, 4.50; N, 4.10.  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  9.04 – 8.92 (m, 1H), 8.36 (s,  
15 1H, N-H), 7.93 – 7.56 (m, 6H), 7.56 – 7.32 (m, 6H), 7.32 – 7.12 (m, 4H), 6.97 – 6.83 (m, 1H), 4.15 – 4.07 (m, 2H), 3.82 – 3.64 (m, 1H), 3.52 – 3.36 (m, 1H), 1.55 (s, 3H), 1.25 (s, 3H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  205.0 (d,  $J = 16.5$  Hz), 176.5, 176.2, 168.5 (d,  $J = 5.7$  Hz), 161.3, 151.7, 138.3, 137.9, 135.8 (d,  $J = 8.7$  Hz), 134.6 (d,  $J = 9.9$  Hz), 134.1, 134.1 (d,  $J = 10.3$  Hz), 132.6 (d,  $J = 6.3$  Hz), 131.5 (d,  $J = 2.1$  Hz), 130.8 (d,  $J = 2.6$   
20 Hz), 130.7 (d,  $J = 3.6$  Hz), 130.0, 129.4, 128.7 (d,  $J = 10.3$  Hz), 128.2 (d,  $J = 10.5$  Hz), 125.1 (d,  $J = 2.8$  Hz), 122.8 (d,  $J = 2.3$  Hz), 63.5, 37.2, 24.4, 23.6.  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  49.0. IR (cm $^{-1}$ ): 1940, 1626, 1607.

Example 37: catalytic reduction by transfer hydrogenation of ketones and aldehydes with complexes of examples 1-39.

25 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  $\mu$ L of the previously prepared solution containing the catalyst and 200  $\mu$ L of a 0.1 M sodium isopropoxide solution in 2-propanol were added successively to a ketone or aldehyde  
30 solution (1 mmol) in 10 mL of 2-propanol under reflux (S/C = 1000, S/B = 50).

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 (S/C = 1000, L/C = 5, S/B = 50).

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 50000/1 while the molar ratio substrate/base was in the range of 10/1 to 100/1.

- 5 The reaction temperature was kept at 82 °C.

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 1-39 and NaOiPr or K<sub>2</sub>CO<sub>3</sub> as base**

Complex	S/C	Ligand	Base (S/B)	Conversion		
				% (min)	TOF (h <sup>-1</sup> ) <sup>a</sup>	ee (%)
1	1000	-	NaOiPr (50/1)	54 (90)	-	
2	1000	-	NaOiPr (50/1)	42 (60)	-	
3	1000	-	NaOiPr (50/1)	27 (90)		
4+5	1000	-	NaOiPr (50/1)	81 (90)		
6+7	1000	-	NaOiPr (50/1)	95 (90)		
8	1000	-	NaOiPr (50/1)	90 (90)		
9	1000	-	NaOiPr (50/1)	88 (90)		
16	1000	-	NaOiPr (50/1)	100 (2)	12000	
16	10000	-	NaOiPr (50/1)	100 (36)	8000	
18	10000	-	NaOiPr (50/1)	100 (17)	20000	
20	10000	-	NaOiPr (50/1)	100 (0.06)	86000	
20	50000	-	NaOiPr (50/1)	100 (0.45)	55000	
21	1000	-	K <sub>2</sub> CO <sub>3</sub> (20/1)	95 (30)		
21	1000	-	NaOiPr (50/1)	96 (15)		
22	10000	-	NaOiPr (50/1)	100 (17)	18000	
27	1000	en	NaOiPr (50/1)	25 (120)	-	
27	1000	ampy	NaOiPr (50/1)	38 (120)	-	
28	1000	en	NaOiPr (50/1)	44 (120)	-	
28	1000	ampy	NaOiPr (50/1)	90 (120)	3500	
29	1000	en	NaOiPr (50/1)	74 (120)	400	13
29	1000	ampy	NaOiPr (50/1)	95 (120)	1700	17
29	1000	(±)iPr-ampy	NaOiPr (50/1)	97 (30)	6700	17
29	1000	(R,R)-DPEN	NaOiPr (50/1)	96 (120)	1200	59
29	1000	(S,S)-DPEN	NaOiPr (50/1)	94 (120)	700	32
30	1000	en	NaOiPr (50/1)	92 (120)	900	22
30	1000	ampy	NaOiPr (50/1)	88 (300)	300	18

<b>30</b>	1000	(±)iPr-ampy	NaO <i>i</i> Pr (50/1)	97 (120)	1200	25
<b>30</b>	1000	(R,R)-DPEN	NaO <i>i</i> Pr (50/1)	93 (120)	8400	32
<b>30</b>	1000	(S,S)-DPEN	NaO <i>i</i> Pr (50/1)	78 (120)	1100	16
<b>31</b>	1000	en	NaO <i>i</i> Pr (50/1)	48 (120)	-	13
<b>31</b>	1000	ampy	NaO <i>i</i> Pr (50/1)	86 (120)	1800	66
<b>31</b>	1000	(±)iPr-ampy	NaO <i>i</i> Pr (50/1)	95 (30)	5800	67
<b>31</b>	1000	(R,R)-DPEN	NaO <i>i</i> Pr (50/1)	85 (120)	800	46
<b>31</b>	1000	(S,S)-DPEN	NaO <i>i</i> Pr (50/1)	46 (120)	300	53
<b>32</b>	1000	en	NaO <i>i</i> Pr (50/1)	85 (120)	3700	
<b>32</b>	1000	ampy	NaO <i>i</i> Pr (50/1)	93 (120)	7400	
<b>33</b>	1000	en	NaO <i>i</i> Pr (50/1)	46 (120)	-	
<b>33</b>	1000	ampy	NaO <i>i</i> Pr (50/1)	72 (120)	6850	
<b>34</b>	1000	en	NaO <i>i</i> Pr (50/1)	91 (120)	1200	9
<b>34</b>	1000	ampy	NaO <i>i</i> Pr (50/1)	94 (30)	10650	2
<b>34</b>	1000	(±)iPr-ampy	NaO <i>i</i> Pr (50/1)	94 (5)	16000	22
<b>34</b>	1000	(R,R)-DPEN	NaO <i>i</i> Pr (50/1)	96 (30)	16000	23
<b>34</b>	1000	(S,S)-DPEN	NaO <i>i</i> Pr (50/1)	96 (30)	16000	1
<b>35</b>	1000	en	NaO <i>i</i> Pr (50/1)	97 (30)	6000	18
<b>35</b>	1000	ampy	NaO <i>i</i> Pr (50/1)	94 (5)	16800	23
<b>35</b>	1000	(±)iPr-ampy	NaO <i>i</i> Pr (50/1)	97 (5)	19200	24
<b>35</b>	1000	(R,R)-DPEN	NaO <i>i</i> Pr (50/1)	97 (5)	15000	30
<b>35</b>	1000	(S,S)-DPEN	NaO <i>i</i> Pr (50/1)	96 (5)	12000	19
<b>36</b>	1000	en	NaO <i>i</i> Pr (50/1)	91 (30)	10100	25
<b>36</b>	1000	ampy	NaO <i>i</i> Pr (50/1)	95 (30)	10100	25
<b>36</b>	1000	(±)iPr-ampy	NaO <i>i</i> Pr (50/1)	90 (5)	15100	39
<b>36</b>	1000	(R,R)-DPEN	NaO <i>i</i> Pr (50/1)	97 (30)	17700	12
<b>36</b>	1000	(S,S)-DPEN	NaO <i>i</i> Pr (50/1)	92 (30)	15200	26
<b>39</b>	1000	-	NaO <i>i</i> Pr (50/1)	96 (30)	13900	-

<sup>a</sup> TOF = turnover frequency (moles of carbonyl compound converted to alcohol per mole of catalyst per hour) at 50% conversion.

**Table 3. Catalytic transfer hydrogenation of ketones and aldehydes (0.1 M) to alcohols with the complexes 1-21 using a ratio substrate/base (NaOiPr) of 50/1**

Complex	Substrate	S/C	Conversion % (min)
1	benzaldehyde	1000	11 (10)
3	benzaldehyde	1000	10 (10)
4+5	benzaldehyde	1000	8 (30)
6+7	benzophenone	1000	92 (10); 94 (30)
6+7	benzaldehyde	1000	14 (60)
6+7	4-bromobenzaldehyde	1000	30 (60)
8	benzaldehyde	1000	25 (60)
9	benzaldehyde	1000	20 (60)
20	4-bromobenzaldehyde	1000	97 (10)
20	( <i>E</i> )-2-methyl-3-phenylacrylaldehyde	1000	93 (40)
21	benzophenone	1000	94 (30)
21	benzaldehyde	1000	98 (60)

*Example 38:* catalytic reduction of ketones with complexes of examples 1-36 using molecular hydrogen

The hydrogenation reactions were performed in an 8 vessels Endeavor Parr apparatus. The vessels were charge with the catalysts (2.5  $\mu$ mol). The vessels were closed, charged with 5 bar of N<sub>2</sub> and slowly vented five times. The ketone (5 mmol), optionally ligand (5  $\mu$ mol), the solvent (0.9 mL) and 1 mL of a solution of *t*-BuOK 0.1 M were added. The vessels were charged with 20 bar of H<sub>2</sub> and slowly vented four times. The vessel was charged to 30 bars and heated to 70 °C (S/C = 2000, S/B = 50, L/C = 2).

The molar ratio of substrate/catalyst varied from 2000/1 to 25000/1 while the molar substrate/base ratio range from 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.

For the in situ reactions, the vessel was charge with the precursor catalyst (2.5  $\mu$ mol) and the corresponding ligand (5  $\mu$ mol) (L/C = 2/1) (see Tables 4 and 5).

**Table 4. Catalytic hydrogenation (30 bar) of acetophenone to 1-phenylethanol in the presence of the complexes 1-25 using *t*-BuOK or KOH as base**

Complex	S/C	ligand	solvent	Base (S/B)	conversion %(h)
1	2000	-	EtOH	<i>t</i> -BuOK (50/1)	100 (16)
2	2000	-	EtOH	<i>t</i> -BuOK (50/1)	100 (16)
3	2000	-	EtOH	<i>t</i> -BuOK (50/1)	100 (16)
8	2000	-	EtOH	<i>t</i> -BuOK (50/1)	100 (16)
16	2000	-	MeOH	<i>t</i> -BuOK (20/1)	63 (16)
17	2000	-	MeOH	<i>t</i> -BuOK (20/1)	100 (16)
20	2000	-	EtOH	<i>t</i> -BuOK (50/1)	61 (16)
20	2000	-	MeOH	<i>t</i> -BuOK (20/1)	25 (16)
21	2000	-	EtOH	<i>t</i> -BuOK (50/1)	43 (16)
21	2000	-	MeOH	<i>t</i> -BuOK (20/1)	13 (16)
22	2000	-	EtOH	<i>t</i> -BuOK (50/1)	42 (16)
22	2000	-	MeOH	<i>t</i> -BuOK (20/1)	36 (16)
25	2000	-	EtOH	<i>t</i> -BuOK (50/1)	72 (16)
25	2000	en	EtOH	<i>t</i> -BuOK (50/1)	100 (16)
25	2000	ampy	EtOH	<i>t</i> -BuOK (50/1)	100 (16)
25	10000	en	EtOH	<i>t</i> -BuOK (50/1)	100 (16)
25	10000	ampy	EtOH	<i>t</i> -BuOK (50/1)	92 (16)
25	10000	en	MeOH	<i>t</i> -BuOK (50/1)	28 (16)
25	10000	ampy	MeOH	<i>t</i> -BuOK (50/1)	81 (16)
25	10000	en	MeOH	KOH (50/1)	27 (16)
25	10000	ampy	MeOH	KOH (50/1)	91 (16)
25	25000	en	MeOH	KOH (50/1)	15 (16)
25	25000	ampy	MeOH	KOH (50/1)	45 (16)

**Table 5. Catalytic hydrogenation (30 bar) of ketones to alcohols in the presence of the complexes 1-25 in ethanol using a ratio substrate/*t*-BuOK of 50/1**

Complex	Ketone	S/C	Ligand	Conversion % (h)
2	tetralone	10000		8 (16)
2	2'-Me-acetophenone	10000		100 (16)
2	4'-MeO-acetophenone	500		100 (3)
2	4'-NO <sub>2</sub> -acetophenone	10000		10 (16)
2	benzophenone	500		100 (3)
2	benzoin	10000		5 (16)
2	2'-Cl-acetophenone	10000		100 (16)
8	tetralone	10000		4 (16)
8	2'-Me-acetophenone	10000		28 (16)
8	4'-MeO-acetophenone	500		75 (3)
8	4'-NO <sub>2</sub> -acetophenone	10000		1 (16)
8	benzophenone	500		100 (3)
8	benzoin	10000		9 (16)
8	2'-Cl-acetophenone	10000		100 (16)
16	tetralone	10000		2 (16)
16	2'-Me-acetophenone	10000		76 (16)
16	4'-MeO-acetophenone	500		76 (3)
16	4'-NO <sub>2</sub> -acetophenone	10000		5 (16)
16	benzophenone	500		99 (3)
16	benzoin	10000		7 (16)
16	2'-Cl-acetophenone	10000		84 (16)
25	2-octanone	1000	ampy	36 (3)
25	isobutyrophenone	1000	ampy	61 (3)
25	tetralone	10000	ampy	7 (16)
25	tetralone	10000	en	3 (16)
25	2'-Me-acetophenone	10000	ampy	38 (16)
25	2'-Me-acetophenone	10000	en	100 (16)



## CLAIMS

1. A pentacoordinate or hexacoordinate complex of formula (1):



5 wherein

M = Ru or Os;

a, b and d are independently 0 or 1;

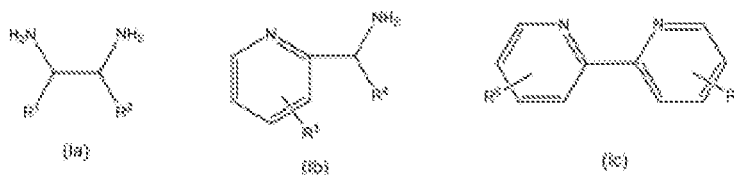
c is 1 or 2;

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

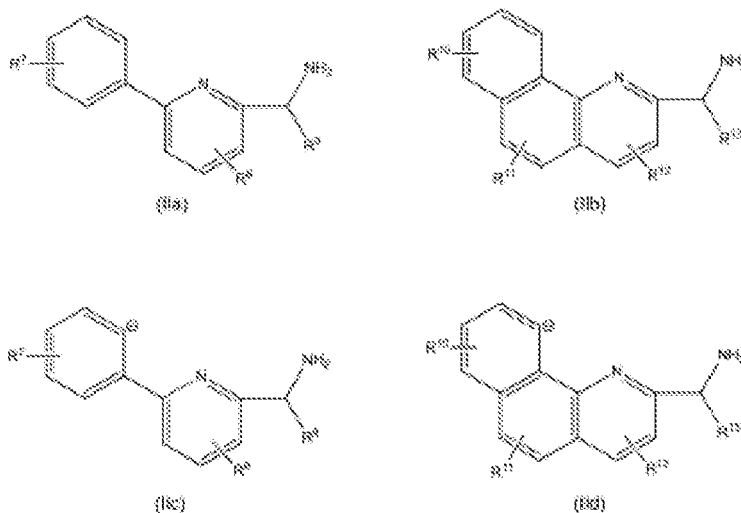
W is selected among halides, C1-C20 carboxylates and C1-C20 alkoxides;

L is a nitrogen-containing ligand selected among:

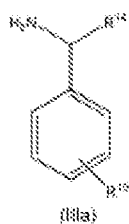
(I) a NN compound of formula Ia to Ic:



15 (II) a HCNN compound of formula IIa – IIb and a CNN compound of formula IIc – IId:



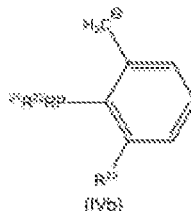
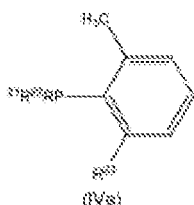
(III) a HCN compound of formula IIIa



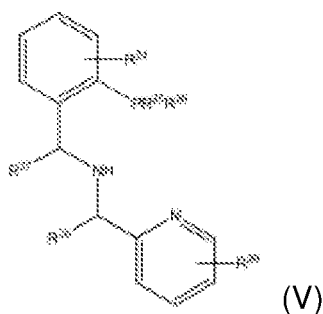
wherein

$R^1 - R^{15}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups;

- 5  $L^1$  is at least one phosphorus-containing ligand selected among:
- a phosphine (P) selected among: a phosphine of formula  $PR^{16}R^{17}R^{18}$ , wherein  $R^{16} - R^{18}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; an optically active phosphine selected among (S)-neomenthylidiphenylphosphine and (R)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-
  - 10 binaphthyl;
  - a diphosphine (PP) selected among: a diphosphine of formula  $P(R^{19})_2 - Z - P(R^{20})_2$ , wherein Z is a C2-C4 aliphatic group 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
  - 15 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}ethylidicyclohexyl phosphine, (R)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethylidicyclohexyl phosphine and (2R,4R)-2,4-
  - 20 bis(diphenylphosphine)pentane;
  - a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



- a PNN compound of formula (V)



wherein

$R^{21} - R^{29}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups;

5 provided that:

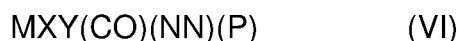
- when  $a = b = c = 1$ ;  $d = 0$ ;  $X = Y = \text{Cl}$ ;  $L = \text{ethylenediamine}$  or 2-(aminomethyl)pyridine or 2,2'-bipyridine or 4,4'-dimethyl-2,2'-bipyridine,  $L'$  is not a phosphine (P) of formula  $\text{PR}^{16}\text{R}^{17}\text{R}^{18}$  in which  $R^{16} = R^{17} = R^{18} = \text{phenyl}$  or *p*-tolyl;

10 - when  $a = 0$ ;  $b = c = d = 1$ ;  $X = W = \text{Cl}$  or  $X = \text{H}$  and  $W = \text{Cl}$ ,  $L = \text{ethylenediamine}$  or 2-(aminomethyl)pyridine,  $L'$  is not  $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{PPh}_2$ ;

- when  $a = d = 0$ ;  $b = c = 1$ ;  $X = \text{Cl}$ ;  $L = \text{ethylenediamine}$  or 2-(aminomethyl)pyridine,  $L'$  is not a ligand (CP) of formula (IVb) in which  $R^{21} = R^{22} = \text{phenyl}$  and  $R^{23} = \text{methyl}$ ; and

- when  $a, b$  and  $d$  are 0,  $c$  is 2,  $X$  is Cl and  $R^{23}$  is  $-\text{CH}_3$ ,  $R^{21}$  and  $R^{22}$  are not phenyl groups.

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



wherein M, X, Y, (NN) and (P) are as defined in claim 1, provided that when X and Y are Cl,  $R^{16} - R^{18}$  are not phenyl or *p*-tolyl groups.

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



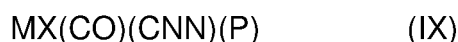
wherein M, X, W, (NN) and (PP) are as defined in claim 1 and provided that when X is Cl or H, (NN) is not ethylenediamine or 2-(aminomethyl)pyridine and the diphosphine (PP) is not  $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{PPh}_2$ .

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



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

5. The complex according to claim 1, of formula (IX)



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

6. The complex according to claim 1, of formula (X)



wherein M, X, (NN) and (CP) are as defined in claim 1 and provided that when X is Cl,

5 (NN) is not ethylenediamine or 2-(aminomethyl)pyridine and (CP) is not a compound of formula (IVb) in which  $\text{R}^{21} = \text{R}^{22} = \text{phenyl}$  and  $\text{R}^{23} = \text{methyl}$ .

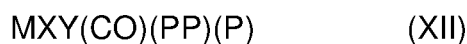
7. The complex according to claim 1, of formula (XI)



wherein M, X, (CP) and (HCP) are as defined in claim 1 and provided that when X is Cl

10 and  $\text{R}^{23}$  is  $-\text{CH}_3$ ,  $\text{R}^{21} - \text{R}^{22}$  are not phenyl groups.

8. The complex according to claim 1, of formula (XII)



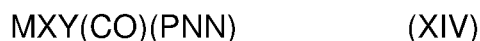
wherein M, X, Y, (PP) and (P) are as defined in claim 1.

9. The complex according to claim 1, of formula (XIII)

15 
$$\text{MXY}(\text{CO})(\text{HCN})(\text{PP}) \quad (\text{XIII})$$

wherein M, X, Y, (HCN) and (PP) are as defined in claim 1.

10. The complex according to claim 1, of formula (XIV)



wherein M, X, Y and (PNN) are as defined in claim 1.

20 11. The complex according to any one of claims 1 to 10, wherein X and Y are equal and are selected among Cl, H, C1-C20 alkoxides and C1-C20 carboxylate group.

12. A process for preparing a complex of formula (VI) comprising reacting a compound of formula  $\text{MXY}(\text{CO})(\text{PPh}_3)_2$ , or of formula  $\text{MXY}(\text{CO})(\text{PPh}_3)_2(\text{dmf})$ , wherein M, X, Y are as defined above and (dmf) is dimethylformamide, with a phosphine (P) selected among:

- phosphines 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 group and C5-C20 aromatic groups; and

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

30 and at least one nitrogen-containing compound NN selected among



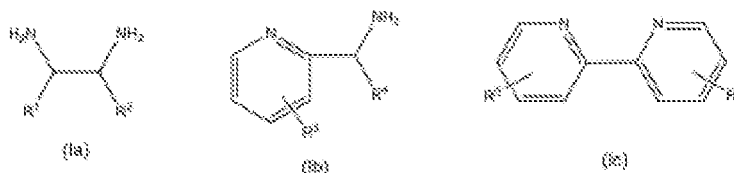
wherein

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

13. A process for preparing a complex of formula (VII) comprising reacting  $[MXY(CO)_2]_n$ ,  $MXY(CO)(PPh_3)_2$  or  $MXY(CO)(PPh_3)_2(dmf)$ , wherein M, X and Y are as defined above and (dmf) is dimethylformamide, with a diphosphine (PP) selected among:

- a diphosphine of formula  $P(R^{19})_2 - Z - P(R^{20})_2$ , wherein Z is a C2-C4 aliphatic group 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; and
- 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;

and at least one nitrogen-containing compound NN selected among:

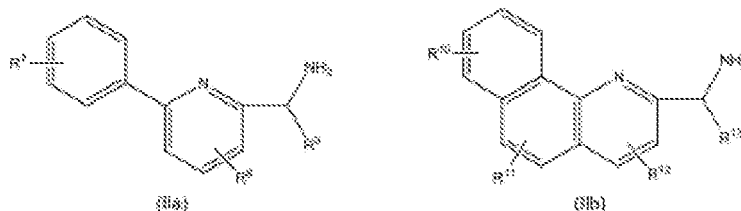


wherein

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

14. A process for preparing a complex of formula (VIII) comprising reacting a compound of formula  $MXY(CO)(PPh_3)_2$ , or of formula  $MXY(CO)(PPh_3)_2(dmf)$ , wherein M, X, Y are

as defined above and (dmf) is dimethylformamide, with a nitrogen-containing compound (HCNN) selected among:

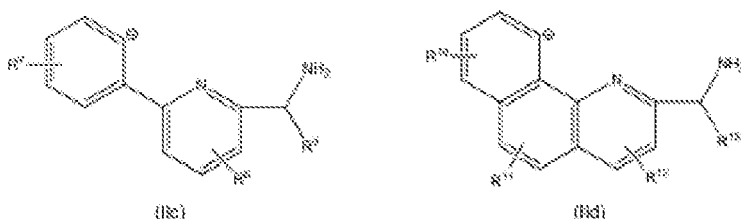


wherein

- 5  $R^7 - R^{13}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, and optionally with a phosphine (P) selected among:
- a phosphine of formula  $PR^{16}R^{17}R^{18}$ , wherein  $R^{16} - R^{18}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; and
  - an optically active phosphine selected among (*S*)-neomenthylidiphenylphosphine and
- 10 (*R*)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl.

15. A process for preparing a complex of formula (IX) by

- (i) reacting a compound of formula  $MX_3(PPh_3)_3$ , wherein M, X and Y are as described above, with a nitrogen-containing ligand (CNN) of formula (IIc) or (IId)



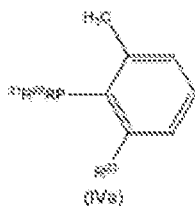
15 wherein

- $R^7 - R^{13}$  are independently selected among H, C1-C20 aliphatic group and C5-C20 aromatic group, and optionally a phosphine (P) selected among:
- a phosphine of formula  $PR^{16}R^{17}R^{18}$ , wherein  $R^{16} - R^{18}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups;
- 20 - an optically active phosphine selected among (*S*)-neomenthylidiphenylphosphine and (*R*)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl, thereby obtaining an intermediate derivative and

(ii) reacting said derivative with CO.

16. A process for preparing a complex of formula (X) comprising:

- 25 (i) reacting  $MX_3 \cdot xH_2O$  with a HCP compound of formula (IVa)

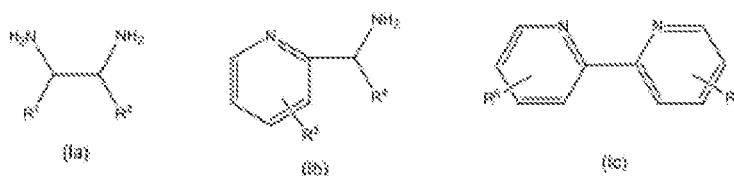


wherein

M and X are as defined above and  $R^{21} - R^{23}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups, thereby obtaining an intermediate

5 complex of formula (XI); and

(ii) reacting the complex of formula (XI) with a (NN) ligand of formula Ia to Ic:

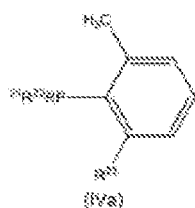


wherein

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

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17. A process for preparing a complex of formula (XI) comprising reacting  $MX_3 \cdot xH_2O$  with a (HCP) compound of formula (IVa)



wherein

M and X are as defined above and  $R^{21} - R^{23}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups.

15

18. A process for preparing a complex of formula (XII) comprising reacting a compound of formula  $MX_3(CO)(PPh_3)_2$ , or of formula  $MX_3(CO)(PPh_3)_2(dmf)$ , wherein M, X, Y are as defined above and (dmf) is dimethylformamide, with a phosphine (P) selected

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among:

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

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

and a diphosphine (PP) selected among:

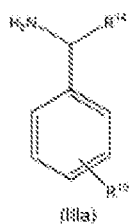
- 5 - a diphosphine of formula  $P(R^{19})_2 - Z - P(R^{20})_2$ , wherein Z is a C2-C4 aliphatic group or ferrocene optionally substituted with C1-C20 aliphatic groups, and wherein R<sup>19</sup> and R<sup>20</sup> are independently selected among C1-C20 aliphatic groups and C5-C20 aromatic groups;
- 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}ethylcyclohexyl phosphine, (*R*)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethylcyclohexyl phosphine and (2*R*,4*R*)-2,4-bis(diphenylphosphine)pentanemethoxyphenyl)phosphine]ferrocenyl}ethylcyclohexyl phosphine and (2*R*,4*R*)-2,4-bis(diphenylphosphine)pentane.

19. A process for preparing a compound of formula (XIII) comprising reacting a compound of formula  $MXY(CO)(PPh_3)_2$ , or of formula  $MXY(CO)(PPh_3)_2(dmf)$ , wherein M, X, Y are as defined above and (dmf) is dimethylformamide, with a diphosphine (PP) selected among:

- 20 - a diphosphine of formula  $P(R^{19})_2 - Z - P(R^{20})_2$ , wherein Z is a C2-C4 aliphatic group or ferrocene optionally substituted with C1-C20 aliphatic groups, and wherein R<sup>19</sup> and R<sup>20</sup> are independently selected among C1-C20 aliphatic groups and C5-C20 aromatic groups;
- 25 - 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}ethylcyclohexyl phosphine, (*R*)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethylcyclohexyl phosphine and (2*R*,4*R*)-2,4-bis(diphenylphosphine)pentane;

and a nitrogen-containing ligand (HCN) of formula IIIa

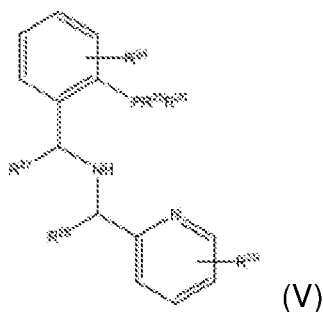




wherein

$R^{14}$  and  $R^{15}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups  
 $R^1 - R^{15}$  are independently selected among H, C1-C20 aliphatic groups  
 5 and C5-C20 aromatic groups.

20. A process for preparing a complex of formula (XIV) comprising reacting a compound of formula  $MXY(CO)(PPh_3)_2$ , or of formula  $MXY(CO)(PPh_3)_2(dmf)$ , wherein M, X, Y are as defined above and (dmf) is dimethylformamide, with a tridentate (PNN) ligand of formula (V)



wherein

$R^{24} - R^{29}$  are independently selected among H, C1-C20 alkyl group and C5-C20 aryl groups.

21. Use of the compounds according to any one of claims 1 to 10 as catalyst or pre-catalyst in the reduction of ketones or aldehydes to alcohols by transfer hydrogenation or hydrogenation with molecular hydrogen.

22. 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 from the group consisting of C3-C42 ketones and C2-C41 aldehydes thereby obtaining a mixture; and  
 20 (b) contacting said mixture with molecular  $H_2$  or with at least one hydrogen-donor, preferably 2-propanol, sodium formate, ammonium formate, a mixture of formic acid and triethylamine,

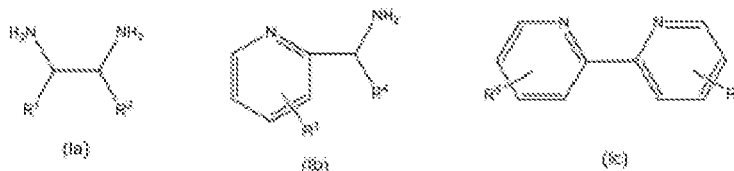
said process being characterized in that the catalyst or pre-catalyst is a pentacoordinate or a hexacoordinate complex of general formula (1):



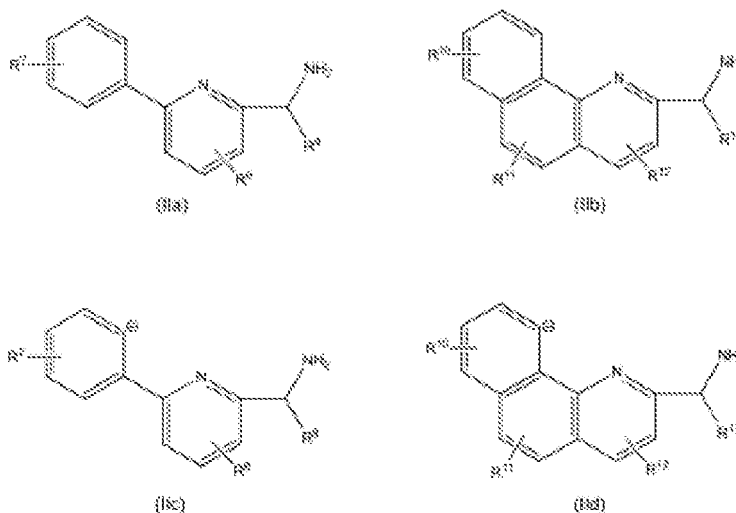
wherein

- 5 M = Ru or Os;  
 a, b and d are independently 0 or 1;  
 c is 1 or 2;  
 X, 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 to Ic:

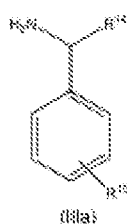


(II) a HCNN compound of formula IIa – IIb and a CNN ligand of formula IIc – IId:



15

(III) a HCN compound of formula IIIa

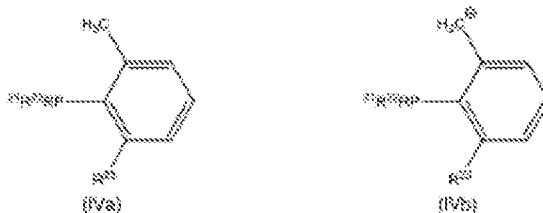


wherein

$R^1 - R^{15}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups;

$L'$  is at least one phosphorus-containing ligand selected among:

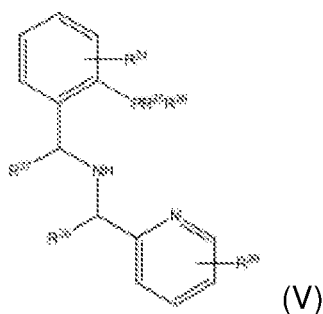
- 5 - a phosphine (P) selected among: a phosphine of formula  $PR^{16}R^{17}R^{18}$ , wherein  $R^{16} - R^{18}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; an optically active phosphine selected among (S)-neomenthylidiphenylphosphine and (R)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl;
- 10 - a diphosphine (PP) selected among: a diphosphine of formula  $P(R^{19})_2 - Z - P(R^{20})_2$ , wherein Z is a C2-C4 aliphatic group 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}ethylcyclohexyl phosphine, (R)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethylcyclohexyl phosphine and (2R,4R)-2,4-bis(diphenylphosphine)pentane;
- 15 - 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;

- 25 - a PNN compound of formula (V)

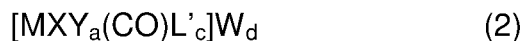


wherein

$R^{24} - R^{29}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups.

- 5 23. The process for the reduction of ketones or aldehydes to the corresponding alcohols according to claim 22, comprising the following steps:
- (a) mixing a pre-catalyst 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 thereby obtaining a mixture; and
- 10 (b) contacting said mixture with molecular  $H_2$  or with at least one hydrogen-donor, preferably 2-propanol, sodium formate, ammonium formate, a mixture of formic acid and triethylamine,

wherein said pre-catalyst has general formula (2):



15 wherein

$M = Ru$  or  $Os$ ;

$a, b$  and  $d$  are independently 0 or 1;

$c$  is 1 or 2;

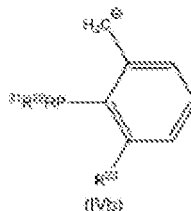
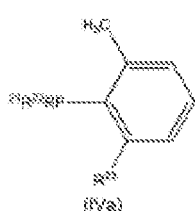
20  $X, Y$  are independently selected among halides, hydride, C1-C20 carboxylates and C1-C20 alkoxides;

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

$L'$  is at least one phosphorus-containing ligand selected among:

- a phosphine (P) selected among: a phosphine of formula  $PR^{16}R^{17}R^{18}$ , wherein  $R^{16} - R^{18}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups; an optically active phosphine selected among (S)-neomenthylidiphenylphosphine and (R)-(+)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl;
- 25

- a diphosphine (PP) selected among: a diphosphine of formula  $P(R^{19})_2 - Z - P(R^{20})_2$ , wherein Z is a C2-C4 aliphatic group 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}ethylcyclohexyl phosphine, (*R*)-1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethylcyclohexyl phosphine and (*2R,4R*)-2,4-bis(diphenylphosphine)pentane;
- a HCP compound of formula (IVa) and a CP ligand of formula (IVb)



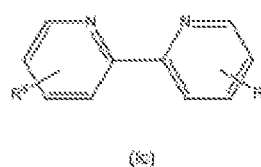
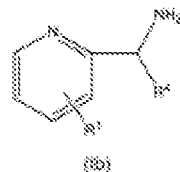
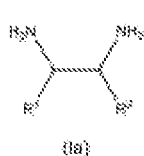
wherein

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

and wherein

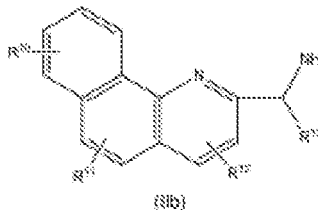
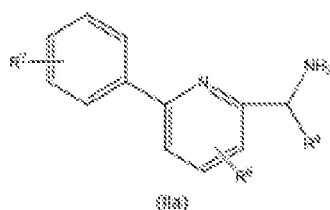
step (a) is carried out by mixing said pre-catalyst with a solution further comprising at least one nitrogen-containing compound L selected among:

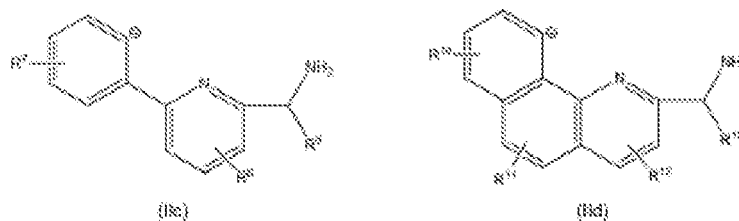
- (i) a NN compound of formula Ia to Ic:



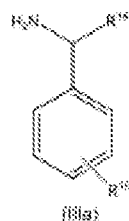
20

- (ii) a HCNN compound of formula IIa – IIb and a CNN ligand of formula IIc – IId:

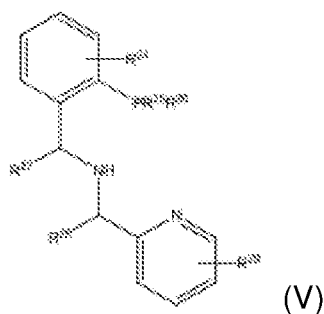




(iii) a HCN compound of formula IIIa



(iv) a PNN compound of formula (V)



5

wherein

$R^1 - R^{15}$  and  $R^{24} - R^{29}$  are independently selected among H, C1-C20 aliphatic groups and C5-C20 aromatic groups.

24. The process according to claim 22 or 23, wherein

- 10 - in step (a) the base is potassium hydroxide, potassium carbonate and an alkali metal alkoxide preferably selected among sodium iso-propoxide, potassium tert-butoxide, more preferably is potassium tert-butoxide; and  
 - in step (b) the mixture is contacted with molecular hydrogen.

25. The process according to claim 22 or 23, wherein in step (a) the base is sodium iso-propoxide and in step (b) the mixture is contacted with at least one hydrogen donor.

- 15 26. The process according to any one of claims 22 to 25, wherein the at least one C3-C41 ketone is selected among compounds of formula  $R^{30}C(=O)R^{31}$ , wherein  $R^{30}$ ,  $R^{31}$  are independently selected among C1-C20 aliphatic, substituted aliphatic, aromatic, substituted aromatic and heteroaromatic groups wherein optionally  $R^{30}$  and  $R^{31}$  are  
 20 linked to form a cycle.

27. The process according to any one of claims 22 to 26, wherein the molar ratio substrate/catalyst or pre-catalyst ranges from 1000/1 to 100000/1, preferably from 1000/1 to 50000/1.

28. The process according to any one of claims 22 to 27, wherein the molar ratio  
5 substrate/base ranges from 10/1 to 100/1.

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2017/050598

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	CAVARZAN DEIVIDI ALEXANDRE ET AL: "Neutral and cationic ruthenium carbonyl complexes [Ru(CO)(2,2'-dipyridylamine)(PR <sub>3</sub> )C <sub>12</sub> ] and [Ru(CO)(N-N)(PPh <sub>3</sub> ) <sub>2</sub> (H)]Cl: synthesis, structural characterization and transfer-hydrogena", TRANSITION METAL CHEMISTRY, CHAPMAN & HALL, GB, vol. 40, no. 1, 31 October 2014 (2014-10-31), pages 117-123, XP035432807, ISSN: 0340-4285, DOI: 10.1007/S11243-014-9896-8 [retrieved on 2014-10-31] complexes 3,4 ----- -/--	1,2, 21-28
<input checked="" type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> 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	Date of mailing of the international search report	
8 March 2017	16/05/2017	
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  Diederren, Jeroen	



## INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2017/050598

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>PRASHANT KUMAR ET AL: "Synthesis and characterization of ruthenium(II) complexes based on diphenyl-2-pyridylphosphine and their applications in transfer hydrogenation of ketones", INORGANICA CHIMICA ACTA, ELSEVIER BV, NL, vol. 368, no. 1, 21 December 2010 (2010-12-21), pages 124-131, XP028182335, ISSN: 0020-1693, DOI: 10.1016/J.ICA.2010.12.057 [retrieved on 2010-12-30] complexes 3,6</p>	1,2, 21-28
X	<p>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 claim 4</p>	1,7, 21-28
X	<p>BARUN BERA ET AL: "Dynamics of H-atom exchange in stable cis-dihydrogen/hydride complexes of ruthenium(ii) bearing phosphine and N-N bidentate ligands", DALTON TRANSACTIONS: THE INTERNATIONAL JOURNAL FOR INORGANIC, ORGANOMETALLIC AND BIOINORGANIC CHEMISTRY, vol. 43, no. 12, 1 January 2014 (2014-01-01), page 4726, XP055297938, GB ISSN: 1477-9226, DOI: 10.1039/c3dt52575a 1b</p>	1,2
X	<p>THANGAVEL SATHIYA KAMATCHI ET AL: "Influence of carboxylic acid functionalities in ruthenium (II) polypyridyl complexes on DNA binding, cytotoxicity and antioxidant activity: Synthesis, structure and in vitro anticancer activity", EUROPEAN JOURNAL OF MEDICINAL CHEMISTRY., vol. 59, 1 January 2013 (2013-01-01), pages 253-264, XP055297941, FR ISSN: 0223-5234, DOI: 10.1016/j.ejmech.2012.11.024 complex 1</p>	1,2

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2017/050598

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

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IB2017/050598

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-28(partially)

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-28(partially)

Compounds of Formula (I) wherein M=Ru for use in hydrogenation of ketones or aldehydes

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2. claims: 1-28(partially)

Compounds of Formula (I) wherein M=Os for use in hydrogenation of ketones or aldehydes

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