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(71) Applicant *(for all designated States except US)*: **KANATA CHEMICAL TECHNOLOGIES INC.** [CA/CA]; MaRs Centre, South Tower, 230-101 College St., Toronto, Ontario M5G 1L7 (CA).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **ABDUR-RASHID, Kamaluddin** [CA/CA]; 3414 Joan Drive, Mississauga, Ontario L5B 1T5 (CA). **AMOROSO, Dino** [CA/CA]; 166 Voyager Pass, Binbrook, Ontario L0R 1C0 (CA). **GUO, Rongwei** [CN/CA]; 1003-2250 Homelands Drive, Mississauga, Ontario L5K 1G8 (CA). **CHEN, Xuanhua** [CN/CA]; 1003-2250 Homelands Drive, Mississauga, Ontario L5K 1G8 (CA). **SUI-SENG, Christine** [CA/CA]; 201-206 St. George Street, Toronto, Ontario M5R 2N6 (CA). **TSANG, Chi-Wing** [CA/CA]; 1501-55 Bloor Street East, Toronto, Ontario M4W 1A9 (CA). **JIA, Wenli** [CN/CA]; 603-2250 Homelands Drive, Mississauga, Ontario L5K 1G8 (CA).

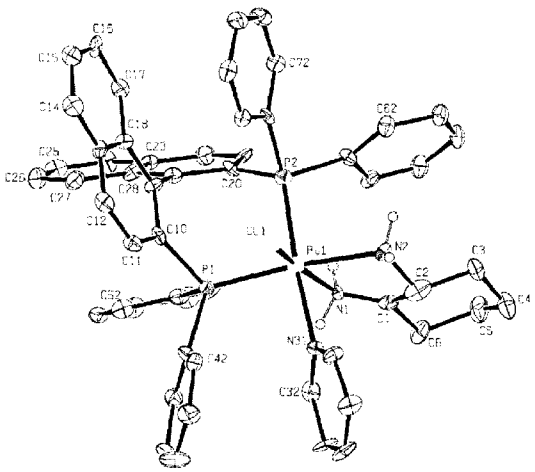
(74) Agent: **BERESKIN & PARR**; 40 King Street West, 40th Floor, Toronto, Ontario M5H 3Y2 (CA).

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*[Continued on next page]*

(54) Title: CATIONIC TRANSITION METAL CATALYSTS

FIGURE 1



$[M(P_2)(PN)X_q(LB)_n]^{r+}[Y^-]_r$ (I)

$[M(PN)_2X_q(LB)_n]^{r+}[Y^-]_r$ (II)

$[M(P)_m(N_2)X_q(LB)_n]^{r+}[Y^-]_r$ (III)

$[M(PNNP)X_q(LB)_n]^{r+}[Y^-]_r$ (IV) and

$[M(P_2)(N_2)X_q(LB)_n]^{r+}[Y^-]_r$ (V)

(57) Abstract: The present disclosure includes catiomc complexes of iron, ruthenium, and osmium, and their use as catalysts in organic synthesis transformations including the hydrogenation of unsaturated compounds. The complexes are represented by the following formulae I, II, III, IV, and V, wherein M is Fe, Ru or Os, P is a monodentate ligand with a phosphorus donor atom, P2 is a bidentate neutral ligand with two phosphorus donor atoms, $N_2$ is a bidentate neutral ligand with two nitrogen donor atoms, PN is a bidentate neutral ligand with phosphorus and nitrogen donor atoms, PNNP is a tetradentate neutral ligand bonded to M via two phosphorus and two nitrogen atoms, X is any anionic ligand, LB is any neutral Lewis base, Y is any non-coordmatmg anion, n is 0, 1, or 2, m is 1 or 2, q is 0 or 1, r is 1 or 2 and q + r = 2.

WO 2009/055912 A1

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TITLE: CATIONIC TRANSITION METAL CATALYSTS

FIELD OF THE DISCLOSURE

The present disclosure relates to the field of catalytic reactions, in which a catalytic system comprising a cationic metal complex is used for organic chemical synthesis, for example, but not limited to the hydrogenation or reduction of compounds containing a carbon-carbon (C=C) or a carbon-heteroatom (C=O, C=N) double bond.

BACKGROUND OF THE DISCLOSURE

The catalysis approach towards synthesis offers several distinct advantages (*e.g.* cost savings, less waste generation) over more traditional protocols using stoichiometric reagents. In particular, transition metal (TM) catalysis has revolutionized organic synthesis (Tsuji, J. *Transition Metal Reagens and Catalysts*; Wiley: West Sussex, England, 2002). The near constant improvement in the field of TM catalysis is undoubtedly due in large part to the introduction of new and improved ligands, which allows for desired transformations to be carried out in a more efficient manner (*i.e.* milder conditions, lower catalyst loadings, higher yields and higher enantioselectivities when applicable).

Catalytic hydrogenation is one of the fundamental reactions in chemistry, and is used in a large number of chemical processes. It is now recognized that catalytic hydrogenations of carbon-carbon double bonds of alkenes, and carbon-heteroatom double bonds of ketones, aldehydes and imines are indispensable processes for the production of the wide range of alkanes, alcohols and amines, including chiral compounds, which are useful as valuable end products and precursors for the pharmaceutical, agrochemical, flavor, fragrance, material and fine chemical industries.

Amongst the several different kinds of processes known to achieve such transformation, two important types are: (a) transfer hydrogenation processes, in which hydrogen-donors such as secondary alcohols, and in particular isopropanol ($^{i}$PrOH), and triethlammonium formate (HCOOH/$NEt_3$) are used, (b) hydrogenation processes, in which molecular hydrogen is used. Both hydrogen transfer and

hydrogenation processes need a catalyst or catalytic system to activate the reducing agent, such as an alcohol, $HCOOH/NEt_3$ or molecular hydrogen.

The catalytic hydrogenation processes developed by Noyori and coworkers (Ohkuma et al., *J. Am. Chem. Soc.*, 1995, 107, 2675 and 10417) are very attractive, since the catalysts consist of air-stable ruthenium complexes of the type $RuCl_2(PR_3)_2$(diamine) and $RuCl_2$(diphosphine)(diamine) which are precursors for the generation of what appears to be some of the most active catalysts for the homogeneous and asymmetric hydrogenation of ketones and imines in the presence of a base and hydrogen gas. It has been proposed and subsequently mechanistically elucidated that the key molecular recognition feature of these catalysts is the presence of mutually cis N–H and Ru–H moieties of the catalytic dihydride species ($RuH_2(PR_3)_2$(diamine) and $RuH_2$(diphosphine)(diamine)) that electronically bind and activate the substrate and facilitate reduction.

Other reactions for which transition metal catalysts have found significant applications include hydroformylations, hydrosilylations, hydroborations, hydroaminations, hydrovinylations, hydroarylations, hydrations, oxidations, epoxidations, reductions, C-C and C-X bond formations (includes reactions such as Heck, Suzuki-Miyaura, Negishi, Buchwald-Hartwig Amination, α-Ketone Arylation, N-Aryl Amination, Murahashi, Kumada, Negishi and Stille reactions etc.), functional group interconversions, kinetic resolutions, dynamic kinetic resolutions, cycloadditions, Diels-Alder reactions, retro-Diels-Alder reactions, sigmatropic rearrangements, electrocyclic reactions, ring-opening and/or ring-closing olefin metatheses, carbonylations, and aziridinations.

SUMMARY OF THE DISCLOSURE

The hydrogenation of ketones has been successfully and advantageously performed using cationic salts of certain neutral Fe(II), Ru(II) and Os(II) complexes. The cationic complexes were prepared by treatment of the neutral precursors with anion abstracting agents. The resulting complexes are air and moisture stable. Solutions can be prepared and handled in air with no obvious signs of decay. The activity of the cationic complexes matches that of the neutral precursors. In several cases, the cationic derivatives give products with improved enantiomeric excess relative to the neutral congener.

Accordingly, the present disclosure provides a compound selected from a compound of Formula I, II, III, IV and V:

$[M(P_2)(PN)X_q(LB)_n]^{r+}[Y^-]_r$ (I)

$[M(PN)_2X_q(LB)_n]^{r+}[Y^-]_r$ (II)

$[M(P)_m(N_2)X_q(LB)_n]^{r+}[Y^-]_r$ (III)

$[M(PNNP)X_q(LB)_n]^{r+}[Y^-]_r$ (IV) and

$[M(P_2)(N_2)X_q(LB)_n]^{r+}[Y^-]_r$ (V)

wherein

M is Fe, Ru or Os;

P is a monodentate ligand bonded to M via a phosphorus atom;

$P_2$ is a bidentate neutral ligand bonded to M via two phosphorus atoms;

$N_2$ is a bidentate neutral ligand bonded to M via two nitrogen atoms;

PN is a bidentate neutral ligand bonded to M via a phosphorus atom and a nitrogen atom;

PNNP is a tetradentate neutral ligand bonded to M via two phosphorus and two nitrogen atoms;

X is any anionic ligand;

LB is any neutral Lewis base;

Y is any non-coordinating anion;

n is 0, 1 or 2;

m is 1 or 2; and

q is 0 or 1;

r is 1 or 2; and

$q + r = 2$.

Also included in the present disclosure is a process for preparing a compound of the disclosure comprising combining a precursor metal compound, an anion abstracting agent, and one or more P, $P_2$, $N_2$, PN or PNNP ligands, and optionally a base and reacting under conditions to form the compound of the disclosure and optionally isolating the compound of the disclosure.

The present disclosure also includes a method for catalyzing a synthetic organic reaction comprising combining starting materials for the reaction with a compound according to the disclosure under conditions for performing the reaction.

The present disclosure also includes the use of a compound of the disclosure for catalyzing a synthetic organic reaction.

The synthetic organic transformations to which the compounds of the disclosure can be applied include but are not limited to: hydrogenations, transfer hydrogenations, hydroformylations, hydrosilylations, hydroborations, hydroaminations, hydrovinylations, hydroarylations, hydrations, oxidations, epoxidations, reductions, C-C and C-X bond formations (including, for example, Heck, Suzuki-Miyaura, Negishi, Buchwald-Hartwig Amination, α-Ketone Arylation, N-Aryl Amination, Murahashi, Kumada, Negishi and Stille reactions etc.), functional group interconversions, kinetic resolutions, dynamic kinetic resolutions, cycloadditions, Diels-Alder reactions, retro-Diels-Alder reactions, sigmatropic rearrangements, electrocyclic reactions, ring-openings, ring-closings, olefin metatheses, carbonylations, and aziridinations. In all transformations listed above the reactions may or may not be regioselective, chemoselective, stereoselective or diastereoselective.

In an embodiment, the present disclosure relates to a process for the reduction of compounds comprising a carbon-carbon (C=C), carbon-oxygen (C=O) or carbon-nitrogen (C=N) double bond, to the corresponding hydrogenated alkane, alcohol or amine, comprising contacting a compound comprising the C=C, C=O or C=N double bond with a catalyst of the Formula (I), (II), (III), (IV) or (V) under hydrogenation conditions.

Other features and advantages of the present disclosure will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples while indicating preferred embodiments of the disclosure are given by way of illustration only, since various changes and modifications within the spirit and scope of the disclosure will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

The present disclosure will now be described in greater detail with reference to the attached drawings in which:

Figure 1 is an X-ray crystal structure of [RuCl(pyridine)(*R*-binap)(*R,R*-cydn)]$BF_4$. Hydrogen atoms, $BF_4$ anion and two $CHCl_3$ molecules omitted for clarity.

DETAILED DESCRIPTION OF THE DISCLOSURE

(I) DEFINTIONS

The term "$C_{1-n}$alkyl" as used herein means straight and/or branched chain, saturated alkyl radicals containing from one to "n" carbon atoms and includes (depending on the identity of n) methyl, ethyl, propyl, isopropyl, n-butyl, s-butyl, isobutyl, t-butyl, 2,2-dimethylbutyl, n-pentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, n-hexyl and the like, where the variable n is an integer representing the largest number of carbon atoms in the alkyl radical.

The term "$C_{1-n}$alkenyl" as used herein means straight and/or branched chain, unsaturated alkyl radicals containing from one to n carbon atoms and one to three double bonds, and includes (depending on the identity of n) vinyl, allyl, 2-methylprop-1-enyl, but-1-enyl, but-2-enyl, but-3-enyl, 2-methylbut-1-enyl, 2-methylpent-1-enyl, 4-methylpent-1-enyl, 4-methylpent-2-enyl, 2-methylpent-2-enyl, 4-methylpenta-1,3-dienyl, hexen-1-yl and the like, where the variable n is an integer representing the largest number of carbon atoms in the alkenyl radical.

The term "$C_{3-n}$cycloalkyl" as used herein means a monocyclic or polycyclic saturated carbocylic group containing from three to n carbon atoms and includes (depending on the identity of n), cyclopropyl, cyclobutyl, cyclopentyl, cyclodecyl, bicyclo[2.2.2]octane, bicyclo[3.1.1]heptane and the like, where the variable n is an integer representing the largest number of carbon atoms in the cycloalkyl group.

The term "aryl" as used herein means a monocyclic, bicyclic or tricyclic aromatic ring system containing at least one aromatic ring and from 6 to 14 carbon atoms and includes phenyl, naphthyl, anthracenyl, 1,2-dihydronaphthyl, 1,2,3,4-tetrahydronaphthyl, fluorenyl, indanyl, indenyl and the like.

The term "heterocyclic" as used herein means a monocyclic, bicyclic or tricyclic ring system containing from 5 to 14 atoms of which, unless otherwise specified, one, two, three, four or five are heteromoieties independently selected from

N, $NR^a$, $NR^bR^c$, O, S, $SiR^a$ and $SiR^bR^c$, wherein $R^a$ is selected from H, $C_{1-6}$alkyl, =O and OH and $R^b$ and $R^c$ are independently selected from H and $C_{1-6}$alkyl. When the ring system includes at least one aromatic ring it is referred to as "heteroaryl". Heterocylic groups include, for example, thienyl, furyl, pyrrolyl, pyrididyl, indolyl, quinolyl, isoquinolyl, tetrahydroquinolyl, benzofuryl, benzothienyl and the like.

The term "halo" as used herein means halogen and includes chloro, fluoro, bromo, iodo and the like.

The term "fluoro-substituted" as used herein means that one or all of the hydrogens on the referenced group is replaced with fluorine.

The suffix "ene" added on to any of the above groups means that the group is divalent, i.e. inserted between two other groups.

The term "ring system" as used herein refers to a carbon-containing ring system, that includes monocycles, fused bicyclic and polycyclic rings, bridged rings and metalocenes. Where specified, the carbons in the rings may be substituted or replaced with heteroatoms.

The term "polycyclic" as used herein means groups that contain more than one ring linked together and includes, for example, groups that contain two (bicyclic), three (tricyclic) or four (quadracyclic) rings. The rings may be linked through a single bond, a single atom (spirocyclic) or through two atoms (fused and bridged).

The term "non-coordinating anion" as used herein refers to an anion which does not formally bond to or share electrons with the metal center in a covalent bond.

The term "joined together" as used herein means that two substituents are linked together via a linker grouping to form a ring system. The linker grouping comprises at least one atom but may also comprise several atoms, for example up to 20 atoms, resulting in the formation of monocyclic and polycyclic ring systems.

The term "compound(s) of the disclosure" means a compound of the Formula (I), (II), (III), (IV) or (V), or mixtures thereof.

In understanding the scope of the present disclosure, the term "comprising" and its derivatives, as used herein, are intended to be open ended terms that specify the presence of the stated features, elements, components, groups,

integers, and/or steps, but do not exclude the presence of other unstated features, elements, components, groups, integers and/or steps. The foregoing also applies to words having similar meanings such as the terms, "including", "having" and their derivatives. Finally, terms of degree such as "substantially", "about" and "approximately" as used herein mean a reasonable amount of deviation of the modified term such that the end result is not significantly changed. These terms of degree should be construed as including a deviation of at least ±5% of the modified term if this deviation would not negate the meaning of the word it modifies.

(II) COMPOUNDS OF THE DISCLOSURE

Rendering the neutral metal complexes of the present disclosure into an ionic pair dramatically altered the behaviour and properties of the original metal complex. These changes may be borne out of changes in structure of the resulting complex, the charged nature of the newly formed ionic complex or they may be a result of qualities imparted by the new counter ion. Regardless of the origin of effect, there were great advantages gained from this approach in the present disclosure.

Removal of any coordinating ligand from the metal complexes of the present disclosure had the effect of introducing a vacant coordination site. In transition-metal catalysis this is often imperative for substrate binding and may indeed be rate limiting with respect to the catalytic cycle. Abstraction of one or two anionic ligands and substituting them with non- or weakly coordinating anions represents one such method for installing a vacant coordination site. In this manner, generating cationic complexes by abstraction of coordinating anionic ligands and substitution with non-coordinating anionic ligands lead to more active catalysts.

The exchange of one or two coordinating anionic ligands with non-coordinating or weakly coordinating ligands resulted in a more electrophilic, cationic metal centre. This increased electrophilicity lead to stronger binding between the metal and nucleophilic substrates. With respect to catalytic processes involving metal-substrate interactions, this has the obvious consequences and is especially beneficial in the case of weaker nucleophiles such as those with electron-withdrawing groups.

Transforming the covalent metal complexes of the present disclosure into ionic salts lead to derivatives which were more stable than their parents. Without wishing to be limited by theory, increased stability is the result of the removal of

electron density from the metal leading to a metal centre which is less readily oxidized. Thus, the ionic salts prepared from neutral precursors were generally more stable to oxidation under atmospheric conditions displaying greater tolerance toward oxygen and moisture and greater storage stability (i.e. shelf-life).

The solubility properties of ionic complexes were also different from their neutral precursors. Generally, ionic complexes tended to be more soluble in polar solvents and less soluble in apolar solvents. Some ionic complexes were also more soluble in aqueous solutions. That being said, the solubility of the ionic complex can be further tuned with the selection of the anion. For instance, highly fluorinated anions tended to impart a high degree of solubility in a broad range of solvents. In fact, many ionic complexes incorporating highly fluorinated anions were more soluble in nonpolar solvents than the corresponding neutral precursor while their solubility in polar solvents remained high owing to the ionic nature of the complex.

The ability to tailor solubility also afforded the ability to control the solid properties of the ionic complex. That is, polar salts could be readily precipitated with nonpolar solvents leading to higher isolated yields and more regular and controllable particle sizes. A corollary to this property is that these ionic catalysts also hold the promise of more facile removal from product mixtures. An obvious benefit when one considers the use of ionic catalysts in applications where low residual metals are imperative.

While rendering a neutral catalyst cationic holds the promise of many critical advantages, the utility of this approach is limited by competence in catalysis of the resulting ionic complex. If the derived ionic catalyst is no longer active in catalysis then the advantages described above are obviously moot. In the present disclosure, the cationic ruthenium catalysts were shown to be excellent hydrogenation catalysts. The activity of the cationic complexes matched that of the neutral precursors and, in several cases, the cationic derivatives gave products with improved enantiomeric excess relative to the neutral congener. While not wishing to be limited by theory, this is likely due to the fact that the cationic complexes disclosed herein are more reliably and reproducibly activated prior to entering the catalytic cycle. That is to say that while all of the complexes are subject to activation, the cationic complexes fare better in this process than the neutral analogues. The activation process, which is

carried out in alcohol solvents and is often irreproducible and unpredictable, is better suited to the cationic complexes since they are soluble in the solvent system while the neutral complexes are either insoluble or moderately soluble. The poor solubility of the neutral compounds means that the activation is often incomplete and can lead to side reactions giving catalytically inactive species or active species which do not retain the desired stereoselectivity.

Accordingly, the present disclosure provides a compound selected from a compound of Formula I, II, III, IV and V:

$[M(P_2)(PN)X_q(LB)_n]^{r+}[Y^-]_r$ (I)

$[M(PN)_2X_q(LB)_n]^{r+}[Y^-]_r$ (II)

$[M(P)_m(N_2)X_q(LB)_n]^{r+}[Y^-]_r$ (III)

$[M(PNNP)X_q(LB)_n]^{r+}[Y^-]_r$ (IV) and

$[M(P_2)(N_2)X_q(LB)_n]^{r+}[Y^-]_r$ (V)

wherein

M is Fe, Ru or Os;

P is a monodentate ligand bonded to M via a phosphorus atom;

$P_2$ is a bidentate neutral ligand bonded to M via two phosphorus atoms;

$N_2$ is a bidentate neutral ligand bonded to M via two nitrogen atoms;

PN is a bidentate neutral ligand bonded to M via a phosphorus atom and a nitrogen atom;

PNNP is a tetradentate neutral ligand bonded to M via two phosphorus and two nitrogen atoms;

X is any anionic ligand;

LB is any neutral Lewis base;

Y is any non-coordinating anion;

n is 0, 1 or 2;

m is 1 or 2;

q is 0 or 1;

r is 1 or 2; and

$q + r = 2$.

In an embodiment of the disclosure, P is a monodentate phosphine ligand of the Formula (VI):

$$PR^1R^2R^3 \qquad (VI)$$

wherein $R^1$, $R^2$ and $R^3$ are independently selected from $C_{6-18}$aryl, $C_{1-20}$alkyl and $C_{3-20}$cycloalkyl, each being optionally substituted with one to five substituents independently selected from $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, halo, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy and $C_{6-14}$aryl. In further embodiments of the disclosure, $R^1$, $R^2$ and $R^3$ are independently selected from phenyl, $C_{1-6}$alkyl and $C_{3-10}$cycloalkyl, each being optionally substituted with one to three substituents independently selected from $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl, halo, $C_{1-4}$alkoxy and fluoro-substituted $C_{1-6}$alkoxy. In further embodiments of the disclosure, $R^1$, $R^2$ and $R^3$ are all cyclohexyl, phenyl, xylyl or tolyl.

In another embodiment of the disclosure, $P_2$ is a bidentate bisphosphino ligand of the Formula (VII):

$$R^4R^5P\text{-}Q^1\text{-}PR^6R^7 \qquad (VII)$$

wherein $R^4$, $R^5$, $R^6$ and $R^7$ are, independently, as defined for $R^1$, $R^2$ and $R^3$, and $Q^1$ is selected from unsubstituted or substituted $C_1$-$C_{10}$alkylene and unsubstituted or substituted $C_1$-$C_8$alkenylene where the substituents on $Q^1$ are independently selected from one or more of $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, halo, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy and unsubstituted or substituted $C_{6-14}$aryl and/or two substituents on $Q^1$ are joined together to form, including the carbon atoms to which they are attached, one or more unsubstituted or substituted 5-20-membered monocyclic, polycyclic, heterocyclic, carbocyclic, saturated, unsaturated or metallocenyl ring systems, and $Q^1$ is chiral or achiral. In further embodiments of the disclosure, $R^4$, $R^5$, $R^6$ and $R^7$ are independently selected from phenyl, $C_{1-6}$alkyl and $C_{3-10}$cycloalkyl, each being optionally substituted with one to three substituents independently selected from $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl, halo, $C_{1-4}$alkoxy and fluoro-substituted $C_{1-4}$alkoxy and $Q^1$ is selected from unsubstituted or substituted

$C_1$-$C_8$alkylene where the substituents on $Q^1$ are independently selected from one to four $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl halo, $C_{1-4}$alkoxy, fluoro-substituted $C_{1-4}$alkoxy, unsubstituted and substituted phenyl and substituted and unsubstituted naphthyl, or two substituents are joined together to form, including the carbon atoms to which they are attached, one or more unsubstituted or substituted phenylene, cyclohexylene, naphthylene, pyridylene or ferrocenylene groups, and $Q^1$ is chiral or achiral. In further embodiments of the disclosure, $R^4$, $R^5$, $R^6$ and $R^7$ are all cyclohexyl, phenyl, xylyl or tolyl. Unless otherwise specified, the term substituted means that one or more, including all, but suitably one to five, of the available hydrogen atoms on a group are replaced with $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-4}$alkyl, halo or $C_{6-14}$aryl. Representative examples of the preparation of bis(phosphino) ligands are found in Gupta, M. et al. Chem. Commun. 1996, 2083-2084; Moulton, C.J. J. Chem. Soc. Dalton, 1976, 1020-1024). Other bis(phosphino) ligands are selected from:

2,2'-bis-(diphenylphosphino)-1,1'-binaphthyl (BINAP);

2,2'-bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl ($H_8$BINAP);

2,2'-bis-(diphenylphosphino)-6,6'-dimethyl-1,1'-binaphthyl (6MeBINAP);

2,2'-bis-(di-p-tolylphosphino)-1-,1'-binaphthyl (Tol-BINAP);

2,2'-bis[bis(3-methylphenyl)phosphino]-1,1'-binaphthyl;

2,2'-bis[bis(3,5-di-tert-butylphenyl)phosphino]-1,1'-binaphthyl;

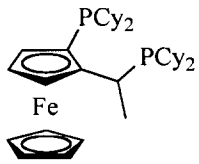
2,2'-bis[bis(4-tert-butylphenyl)phosphino]-1,1'-binaphthyl;

2,2'-bis[bis(3,5-dimethylphenyl)phosphino]-1,1'-binaphthyl (Xyl-BINAP);

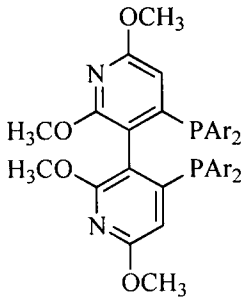
2,2'-bis[bis(3,5-dimethyl-4-methoxyphenyl)phosphino]-1,1'-binaphthyl (Dmanyl-BINAP);

2,2'-bis[bis-(3,5-dimethylphenyl)phosphino]-6,6'-dimethyl-1,1'-binaphthyl (Xyl-6MeBINAP);

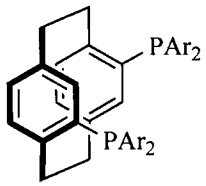
3,3'-bis-(diphenylphosphanyl)-13,13'-dimethyl-12,13,14,15,16,17,12',13',14',15',16',17'-dodecahydro-11H,11'H-[4,4']bi[cyclopenta[a]phenanthrenyl];




wherein Cy is $C_{5-8}$cycloalkyl;




where Ar is phenyl (PPhos), xylyl (XylPPhos) or tolyl (TolPPhos);




where Ar is phenyl (PhanePhos), xylyl (XylPhanePhos) or tolyl (TolPhanePhos); and optical isomers thereof and mixtures of optical isomers in any ratio.

In another embodiment of the disclosure, PN is a ligand of the Formula (VIII):

$$R^8R^9P\text{-}Q^2\text{-}NR^{10}R^{11} \quad \text{(VIII)}$$

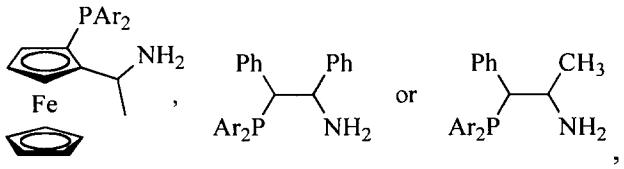
wherein $R^8$ and $R^9$ are, independently as defined for $R^1$-$R^3$;

$Q^2$ is as defined for $Q^1$; and

$R^{10}$ and $R^{11}$ are independently selected from H, $C_{6-18}$aryl, $C_{1-20}$alkyl and $C_{3-10}$cycloalkyl, each being optionally substituted with one to five substituents independently selected from $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl halo, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy and $C_{6-14}$aryl, or

$R^{10}$ and $R^{11}$ are joined to form, together with the nitrogen atom to which they are attached, a saturated, unsaturated or aromatic, monocyclic or polycyclic, substituted or unsubstituted ring system containing from 3 to 14 atoms, or

one of $R^{10}$ or $R^{11}$ are joined with a substituent on $Q^2$ to form, together with the nitrogen atom to which $R^{10}$ and $R^{11}$ is attached, a 4- to 10-membered saturated, unsaturated or aromatic, monocyclic or bicyclic ring system, where if the nitrogen atom is part of aromatic ring or is bonded to an adjacent atom via a double bond, the other of $R^{10}$ and $R^{11}$ is non-existent. In embodiments of the disclosure, $R^8$ and $R^9$ are independently selected from phenyl, $C_{1-6}$alkyl and fluoro-substituted $C_{1-6}$alkyl, with the phenyl being optionally substituted with one to five substituents independently selected from $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl halo, $C_{1-4}$alkoxy and fluoro-substituted $C_{1-4}$alkoxy and $Q^2$ is selected from unsubstituted or substituted $C_1$-$C_8$alkenylene where the substituents on $Q^2$ are independently selected from one to four of $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, halo, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy and unsubstituted or substituted phenyl and/or two substituents on $Q^2$ are joined together to form, including the carbon atoms to which they are attached, one or more unsubstituted or substituted phenylene, naphthylene or ferrocenylene ring systems, and $Q^2$ is chiral or achiral. In further embodiments of the disclosure, $R^8$ and $R^9$ are all phenyl, tolyl or xylyl. In further embodiments, $R^{10}$ and $R^{11}$ and both H. In a further embodiment, one of $R^{10}$ or $R^{11}$ is joined with a substituent on $Q^2$ to form, together with the nitrogen atom to which $R^{10}$ and $R^{11}$ is attached, a substituted or unsubstituted pyridine ring and the other of one of $R^{10}$ or $R^{11}$ is not present. Unless otherwise specified, the term substituted means that one or more, including all, but suitably one to five, of the available hydrogen atoms on a group are replaced with $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy, halo or $C_{6-14}$aryl. Examples of PN ligands, include, for example, $Ph_2PCH_2CH_2NH_2$ (abbreviated as PGly), and:



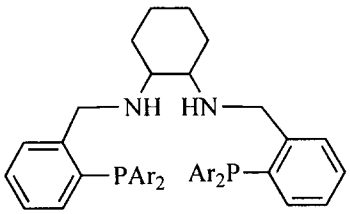
wherein Ar is selected from Ph, tolyl and xylyl, and optical isomers thereof and mixtures of optical isomers.

In a further embodiment of the disclosure, PNNP is a tetradentate diaminodiphosphine of the formula (IXa) or a diiminodiphosphine ligand of the Formula (IXb) :

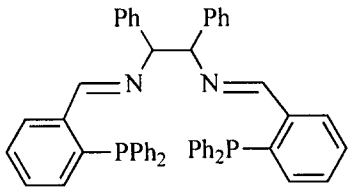
$$R^{12}R^{13}P\text{-}Q^{3}\text{-}NR^{14}\text{-}Q^{4}\text{-}NR^{15}\text{-}Q^{5}\text{-}PR^{16}R^{17} \qquad \text{(IXa)}$$

$$R^{12}R^{13}P\text{-}Q^{3}\text{=}N\text{-}Q^{4}\text{-}N\text{=}Q^{5}\text{-}PR^{16}R^{17} \qquad \text{(IXb)}$$

wherein $R^{12}$, $R^{13}$, $R^{16}$ and $R^{17}$ are independently as defined for $R^{1}$-$R^{3}$, $R^{14}$ and $R^{15}$ are independently as defined for $R^{10}$ and $R^{11}$ and $Q^{3}$, $Q^{4}$ and $Q^{5}$ are independently as defined for $Q^{1}$. In further embodiments of the disclosure, $R^{12}$, $R^{13}$, $R^{16}$ and $R^{17}$ are independently selected from phenyl, $C_{1-6}$alkyl and $C_{3-10}$cycloalkyl, each being optionally substituted with one to five substituents independently selected from $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl, halo, $C_{1-4}$alkoxy and fluoro-substituted $C_{1-6}$alkoxy and $Q^{3}$, $Q^{4}$ and $Q^{5}$ are independently selected from unsubstituted or substituted $C_{1}$-$C_{8}$alkylene and from unsubstituted or substituted $C_{1}$-$C_{8}$alkenylene, where the substituents on $Q^{3}$, $Q^{4}$ and $Q^{5}$ are independently selected from one to four $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl, halo, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy, unsubstituted and substituted phenyl and substituted and unsubstituted naphthyl or two substituents are joined together to form, including the carbon atoms to which they are attached, one or more unsubstituted or substituted phenyl, cyclohexyl, naphthyl or ferrocenyl groups, and $Q^{3}$, $Q^{4}$ and $Q^{5}$ are chiral or achiral. In further embodiments of the disclosure, $R^{12}$, $R^{13}$, $R^{16}$ and $R^{17}$ are all phenyl, tolyl or xylyl. Unless otherwise specified, the term substituted means that one or more, including all, but suitably one to five, of the available hydrogen atoms on a group are replaced with $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy, halo or $C_{6-14}$aryl. Representative examples of the preparation of diaminodiphosphine ligands are found in Li, Y-Y. et al. 2004, 218, 153-156. Exemplary PNNP ligands include:




wherein Ar is phenyl (abbreviated as DPPcydn), tolyl (abbreviated as di(p-tolyl)PPcydn) or xylyl (abbreviated as di(3,5xylyl)PPcydn);




abbreviated as dpen$PPh_2N_2$, and each optical isomer thereof and mixtures of optical isomers.

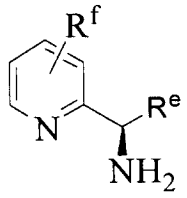
In another embodiment of the disclosure, $N_2$ is a bidentate diamine ligand of the Formula (X):

$$R^{18}R^{19}N\text{-}Q^6\text{-}NR^{20}R^{21} \quad (X)$$

wherein $R^{18}$, $R^{19}$, $R^{20}$ and $R^{21}$ are independently as defined for $R^{10}$ and $R^{11}$ and $Q^6$ is as defined for $Q^1$, or one of $R^{18}$ or $R^{19}$ and/or $R^{20}$ or $R^{21}$ are joined with a substituent on $Q^6$ to form, together with the nitrogen atom to which $R^{18}$, $R^{19}$, $R^{20}$ or $R^{21}$ is attached, a 4- to 10-membered saturated, unsaturated or aromatic, monocyclic or bicyclic, substituted or unsubstituted ring system, where if the nitrogen atom is part of aromatic ring or is bonded to an adjacent atom via a double bond, the other of $R^{18}$ or $R^{19}$ and/or $R^{20}$ or $R^{21}$ is non-existent. In embodiments of the disclosure, $R^{18}$, $R^{19}$, $R^{20}$ and $R^{21}$ are all H and $Q^6$ is selected from unsubstituted or substituted $C_1$-$C_8$alkenylene where the substituents on $Q^6$ are independently selected from one to four of $C_{1\text{-}6}$alkyl, fluoro-substituted $C_{1\text{-}6}$alkyl, halo, $C_{1\text{-}6}$alkoxy, fluoro-substituted $C_{1\text{-}6}$alkoxy and unsubstituted or substituted phenyl and/or two substituents on $Q^6$ are joined together to form, including the carbon atoms to which they are attached, one or more

unsubstituted or substituted phenyl, naphthyl or ferrocenyl ring systems, and $Q^6$ is chiral or achiral. In a further embodiment, one of $R^{18}$ or $R^{19}$ or $R^{20}$ or $R^{21}$ are joined with a substituent on $Q^6$ to form, together with the nitrogen atom to which $R^{18}$, $R^{19}$, $R^{20}$ or $R^{21}$ is attached, a substituted or unsubstituted pyridine ring and the other of one of $R^{18}$ or $R^{19}$ and/or $R^{20}$ or $R^{21}$ is not present. Unless otherwise specified, the term substituted means that one or more, including all, but suitably one to five, of the available hydrogen atoms on a group are replaced with $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy, halo or $C_{6-14}$aryl. Examples of the diamine ligands include, for example, methylenediamine, ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, 2,3-diaminobutane, 1,2-cyclopentanediamine, 1,2-cyclohexanediamine, 1,1-diphenylethylenediamine, 1,1-di(p-methoxyphenyl)ethylenediamine, 1,1-di(3,5-dimethoxyphenyl)ethylenediamine, and 1,1-dinaphthylethylenediamine. Optically active diamine compounds may be also used. Examples thereof include, for example, each optical isomer of 1,2-diphenylethylenediamine (abbreviated name: DPEN), 1,2-di(p-methoxyphenyl)ethylenediamine, 1,2-cyclohexanediamine, 1,2-cycloheptanediamine, 2,3-dimethylbutanediamine, 1-methyl-2,2-diphenylethylenediamine (abbreviated as DACH or CYDN), 1-isobutyl-2,2-diphenylethylenediamine, 1-isopropyl-2,2-diphenylethylenediamine, 1-benzyl-2,2-diphenylethylen-ediamine, 1-methyl-2,2-di(p-methoxyphenyl)ethylenediamine (abbreviated name: DAMEN), 1-isobutyl-2,2-di(p-methoxyphenyl)-ethylenediamine (abbreviated name: DAIBEN), 1-isopropyl-2,2-di(p-methoxyphenyl)ethylenediamine (abbreviated name: DAIPEN), 1-benzyl-2,2-di(p-methoxyphenyl)ethylenediamine, 1-methyl-2,2-di(3,5-dimethoxyphenyl)ethylenediamine, 1-isopropyl-2,2-di(3,5-dimethoxyphenyl)ethylenediamine, 1-isobutyl-2,2-di(3,5-dimethoxy-phenyl)ethylenediamine, 1-benzyl-2,2-di(3,5-dimethoxyphenyl)ethylenediamine, 1-methyl-2,2-dinaphthylethylenediamine, 1-isobutyl-2,2-dinaphthylethylene- diamine, 1-isopropyl-2,2-dinaphthylethylenediamine, and 1-benzyl-2,2-dinaphthylethylenediamine, and mixtures of optical isomers in any ratio. Further, optically active diamine compounds which can be used are not limited to the abovementioned optically active ethylenediamine derivatives. Optically active propanediamine, butanediamine and cyclohexanediamine derivatives may be also

used. In addition, these diamine ligands may be prepared by the process starting from α-amino acids described in the literature (Burrows, C. J., et al., Tetrahedron Letters, 34(12), pp. 1905-1908 (1993)), or by a variety of processes described in the general remark (T. Le Gall, C. Mioskowski, and D. Lucet, Angew. Chem. Int. Ed., 37, pp. 2580-2627 (1998)). In another embodiment of the disclosure, $N_2$ is the bidentate aminopyridine ligand:

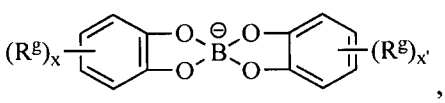


wherein $R^e$ is H, $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl or $C_{6-14}$aryl, $R^f$ is H, halo, $C_{1-6}$alkyl, fluoro-substituted-$C_{1-6}$alkyl, $C_{2-6}$alkenyl, $C_{2-6}$alkynyl, $C_{3-7}$cycloalkyl, $C_{1-6}$alkoxy, fluoro-substituted-$C_{1-6}$alkoxy or $C_{6-14}$aryl, and including each optical isomer thereof and mixtures of optical isomers. In another embodiment, $R^f$ is H, halo, $C_{1-4}$alkyl, fluoro-substituted-$C_{1-4}$alkyl, $C_{2-4}$alkenyl, $C_{2-4}$alkynyl, $C_{3-7}$cycloalkyl, $C_{1-4}$alkoxy, fluoro-substituted-$C_{1-4}$alkoxy or phenyl.

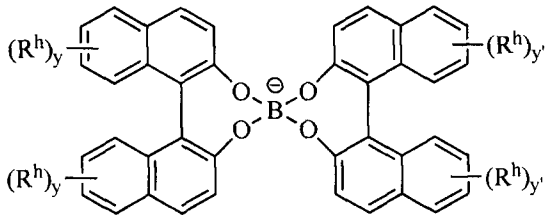
In an embodiment of the disclosure, X is any suitable anionic ligand, including, but not limited to, halo, $C_{1-6}$alkoxy, carboxylate, sulfonates and nitrates. Suitably X is Cl.

LB is any suitable neutral Lewis base, for example any neutral two electron donor, for example acetonitrile, DMF, pyridine, tetrahydrofuran (THF), CO, tBuCN or t-BuNC.

Y is any non-coordinating counter anion, including, but not limited to, OTf, $BF_4$, $PF_6$, $B(C_{1-6}alkyl)_4$, B(fluoro-substituted-$C_{1-6}$alkyl)$_4$ or $B(C_{6-18}aryl)_4$ wherein $C_{6-18}$aryl is unsubstituted or substituted 1-5 times with fluoro, $C_{1-4}$alkyl or fluoro-substituted $C_{1-4}$alkyl. In another embodiment, Y is

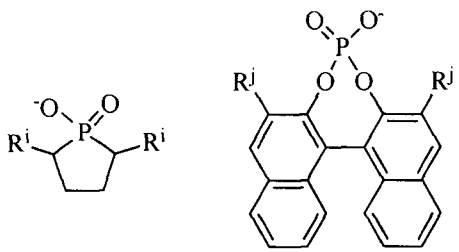


wherein $R^g$ is independently halo, $C_{1-4}$alkyl, fluoro-substituted-$C_{1-4}$alkyl or $C_{6-18}$aryl and x and x' are independently an integer between 1 and 4. In another embodiment, $R^g$ is halo, suitably fluoro. In a further embodiment, Y is



wherein $R^h$ is independently halo, $C_{1-4}$alkyl, fluoro-substituted-$C_{1-4}$alkyl or $C_{6-18}$aryl and y and y' are independently an integer between 1 and 6. In another embodiment, $R^h$ is halo, suitably fluoro. In another embodiment, Y is $Al(C_{1-6}alkyl)_4$, $Al$(fluoro-substituted-$C_{1-6}alkyl)_4$, $Al(C_{6-18}aryl)_4$, $Al(-O-C_{1-6}alkyl)_4$, $Al(-O$-fluoro-substituted-$C_{1-6}alkyl)_4$ or $Al(-O-C_{6-18}aryl)_4$, wherein $C_{6-18}$aryl is unsubstituted or substituted 1-5 times with halo, $C_{1-4}$alkyl or fluoro-substituted $C_{1-4}$alkyl. In afurther embodiment, Y is a carborane or a bromocarborane anion. In another embodiment, the carborane anion is a carborane such as $CB_{11}H_{12}$. In another embodiment, the bromocarborane is a bromocarborane such as $CB_{11}H_6Br_6$.

In a further embodiment, Y is a phosphate anion. In a further embodiment the phosphate anion is of the formula

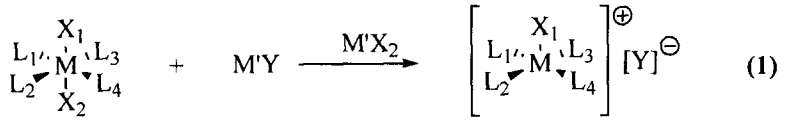


wherein $R^i$ and $R^j$ are independently selected from halo, $C_{1-4}$alkyl, fluoro-substituted-$C_{1-4}$alkyl or $C_{6-18}$aryl.

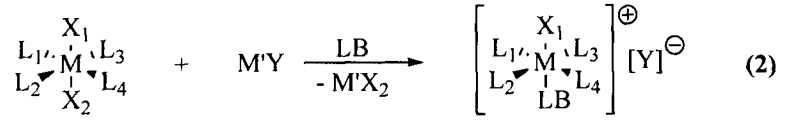
In an embodiment, the anion Y is a chiral compound and is optically pure.

In general, one or two anionic ligands bound to the neutral metal precursor is abstracted by treatment with a salt of a non-coordinating anion (i.e. one which does not formally bond to or share electrons with the metal centre in a typical covalent bond) suitably in an inert atmosphere at ambient or room temperature. This leads to the formation of a salt complex comprised of a formally cationic metal complex and the associated, non- or weakly coordinating anion(s). Exemplified below (Scheme 1, reaction 1) is the use of dichloride ruthenium precursor complexes however this methodology is easily extended to other, non-chloride and other metal-containing precursors. Indeed, any other *halide* precursor can be handled analogously while similar procedures can be employed for *non-halide* precursors such as carboxylates, sulfonates, nitrates etc. Exposure of the resulting cationic complexes to coordinating Lewis Bases, either during the anion abstraction/metathesis reaction or by treatment of the isolated salts, leads to the formation of a coordinatively-saturated metal adduct. In an embodiment, after formation of the cationic catalysts, adducts are formed by the addition of co-ordinating Lewis Bases. This is described in general terms below in reaction 2. The corresponding dicationic complexes (i.e. where both anionic ligands are removed) function in a similar manner.

Scheme 1




(1)




(2)

$X_n$ can be any anionic ligand (n = 1 or 2)
$L_n$ can be any neutral ligand (typically phosphine or amine)
M can be any metal
Y can be any non-coordinating anion
LB (i.e. Lewis Base) can be any neutral two electron donor

In another embodiment, the formation of the compounds of the disclosure is via a procedure wherein a precursor to the neutral complexes, is first rendered cationic or dicationic by treatment with one or two equivalents of a salt of a non-coordinating anion and then treated with the appropriate ligand to generate the compounds of the disclosure. Also, a one-pot procedure can also be envisioned where all of the components are combined to generate the cationic transition-metal complexes.

Accordingly, the present disclosure further includes a process for preparing a compound of the disclosure comprising combining a compound of the formula

$M(P_2)(PN)X_2$ (XI)

$M(PN)_2X_2$ (XII)

$M(P)_m(N_2)X_2$ (XIII)

$M(PNNP)X_2$ (XIV) or

$M(P_2)(N_2)X_2$ (XV)

wherein M, $P_2$, PN, P, PNNP, $P_2$ and X are as defined above, with one or two molar equivalents of an anion abstracting agent and optionally a non- or weakly-coordinating Lewis Base, and reacting under conditions to form the compound of the disclosure and optionally isolating the compound of the disclosure.

In a further embodiment of the present disclosure, there is included a process for preparing a compound of the disclosure comprising combining a precursor metal compound with one or two molar equivalents of an anion abstracting agent, and optionally a Lewis Base and reacting under conditions to form a cationic or dicationic precursor metal compound and combining the cationic or dicationic precursor metal compound with one or more P, $P_2$, $N_2$, PN, or PNNP ligands, as defined above, under conditions to form the compound of the disclosure and optionally isolating the compound of the disclosure.

In an embodiment of the disclosure, the precursor metal compound is of the formula $[MX_2(p\text{-ligand})]_2$ or $MX_2$(ligand) wherein M and X are as defined for the compounds of the disclosure and ligand is any displaceable ligand, for example, *p*-

cymene, benzene, cyclooctadiene (COD) or norbornadiene (NBD), suitably *p*-cymene or norbornadiene (NBD), for example $[MCl_2(p\text{-cymene})]_2$ or $[MCl_2(NBD)]_n$ wherein M is a metal selected from Fe, Ru and Os, in particular ruthenium.

In another embodiment of the disclosure, the precursor metal compound is of the formula $MX_2(P_2)(LB)_n$, wherein M, X, $P_2$ and LB are as defined above and n is 1 or 2. In an embodiment, the precursor metal compound is readily converted into its cationic counterparts $[MX(P_2)(LB)_n]Y$ or $[M(P_2)(LB)_n]Y_2$, by treatment with one or two molar equivalents of an anion abstracting agent as defined above. The corresponding cation is an air stable solid which is isolated in high yields and stored under ambient conditions. A cationic compound of the formula $[MX(P_2)(LB)_n]Y$ or $[M(P_2)(LB)_n]Y_2$ is readily converted into the cationic catalysts of the present disclosure, for example, by reaction with one or more $P_2$, $N_2$ or PN ligands, as defined above. In an embodiment, $(P_2)$ is BINAP and LB is DMF or pyridine. Metal-diphosphine-DMF complexes have been reported in the literature (Noyori et al. Tetrahedron Lett. 1991, 32:4163).

In another embodiment, the anion abstracting agent is a salt of a non-coordinating counter anion Y as defined above. In yet another embodiment, the ligands are selected from one or more of a compound of the Formula (VI), (VII), (VIII), (IX) and (X) as defined above. In another embodiment, the conditions to form the compound of the disclosure comprise reacting at a temperature of about 20°C to about 200 °C, suitably about 50 °C to about 100 °C in a suitable solvent, for about 30 minutes to 48 hours, following by cooling to room temperature. In an embodiment of the disclosure, the compound of the disclosure is isolated using standard techniques, such as by filtration, evaporation of the solvent, recrystallization and/or chromatography, to provide the compound of Formula (I), (II), (III), (IV) or (V).

## (III) PROCESSES UTILIZING THE COMPOUNDS OF THE DISCLOSURE

The compounds of the present disclosure are useful as catalysts in organic synthesis transformations. Accordingly, the present disclosure also includes a method for catalyzing a synthetic organic reaction comprising combining starting materials for the reaction with a compound according to the disclosure under conditions for performing the reaction.

The present disclosure also includes the use of a compound of the disclosure for catalyzing a synthetic organic reaction.

In an embodiment of the disclosure, the synthetic organic reaction is selected from hydrogenation, transfer hydrogenation, hydroformylation, hydrosilylation, hydroboration, hydroamination, hydrovinylation, hydroarylation, hydration, oxidation, epoxidation, reduction, C-C and C-X bond formation (including for example, Heck, Suzuki-Miyaura, Negishi, Buchwald-Hartwig Amination, α-Ketone Arylation, N-Aryl Amination, Murahashi, Kumada, Negishi and Stille reactions), functional group interconversion, kinetic resolution, dynamic kinetic resolution, cycloaddition, Diels-Alder, retro-Diels-Alder, sigmatropic rearrangement, electrocyclic reactiona, ring-opening and/or ring-closing olefin metathesis, carbonylation and aziridination. The reaction conditions for these synthetic transformation are well known to those skilled in the art.

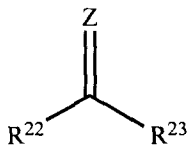
In one particular embodiment of the present disclosure, the compounds of the present disclosure are competent hydrogenation (including transfer hydrogenation) catalysts (as can be seen from the tables of experimental data included herein). The complexes are air and moisture stable. Solutions can be prepared and handled in air with no obvious signs of decay. The activity of the cationic complexes matches that of the neutral precursors. In several cases, the cationic derivatives give products with improved enantiomeric excess relative to the neutral congener (compare entry 27 to 28 and 29 and entry 30 to 31 and 32 in Table 1). While not wishing to be limited by theory, this is likely due to the fact that the cationic complexes disclosed herein are more reliably and reproducibly activated prior to entering the catalytic cycle. That is to say that while all of the complexes are subject to activation, the cationic complexes fare better in this process than the neutral analogues. The activation process, which is carried out in alcohol solvents and is often irreproducible and unpredictable, is better suited to the cationic complexes since they are soluble in the solvent system while the neutral complexes less so. The poor solubility of the neutral compounds means that the activation is often incomplete and can lead to side reactions giving catalytically inactive species or active species which do not retain the desired stereoselectivity.

An interesting result to come out of the derivatization to charged species is in the ligand rearrangement observed in the solid state structure of [RuCl(pyridine)(*R*-binap)(*R,R*-cydn)]$BF_4$ (*vide infra*). The X-ray crystal structure of this compound shows that one of the P atoms of the BINAP ligand is trans to the coordinated pyridine ligand (Figure 1). (It is believed that this is occurs even in the absence of a Lewis base). This is in contrast to the precursor, $RuCl_2$(*R*-binap)(*R,R*-cydn), where both P atoms are trans to the N atoms of the diamine ligand. Such ligand rearrangements are believed to be important processes during activation of the catalysts and may account for superior activity and selectivity of the cationic catalysts relative to their neutral analogues.

Accordingly, the present disclosure relates to a process for the reduction of compounds comprising a carbon-carbon (C=C), carbon-oxygen (C=O) or carbon-nitrogen (C=N) double bond, to the corresponding hydrogenated alkane, alcohol or amine, comprising contacting a compound comprising the C=C, C=O or C=N double bond with a catalyst of the Formula (I), (II), (III), (IV) or (V) under hydrogenation conditions.

The compound comprising a C=C, C=O or C=N, includes compounds having one or more C=C, C=O and/or C=N bonds.

In an embodiment of the invention, the compound comprising a carbon-oxygen (C=O) or carbon-nitrogen (C=N) double bond is a compound of Formula (XI):




(XI)

wherein,

Z is selected from $CR^{24}R^{25}$, $NR^{26}$, $(NR^{26}R^{27})^+D^-$ and O;

$R^{22}$ and $R^{23}$ are simultaneously or independently selected from H, aryl, $C_{1-20}$alkyl, $C_{2-20}$alkenyl, $C_{3-20}$cycloalkyl and heteroaryl, said latter 5 groups being optionally substituted;

$R^{24}$ to $R^{27}$ are independently or simultaneously selected from H, OH, $C_{1-20}$alkoxy, aryloxy, $C_{1-20}$alkyl, $C_{2-20}$alkenyl, $C_{3-20}$cycloalkyl and aryl, said latter 6 groups being optionally substituted;

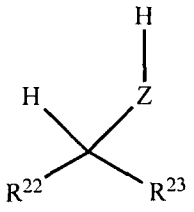
or

one or more of $R^{22}$ to $R^{27}$ are linked to form, together with the atoms to which they are attached, an optionally substituted ring system; and

$D^-$ represents a counteranion,

wherein heteroaryl is a mono- or bicyclic heteroaromatic group containing from 5 to 10 atoms, of which 1-3 atoms is a heteroatom selected from the group consisting of S, O and N, and wherein the optional substituents are selected from the group consisting of halo, OH, $NH_2$, $OR^{28}$, $NR^{28}{}_2$ or $R^{28}$ groups, in which $R^{28}$ is selected from $C_{1-6}$alkyl, $C_{2-6}$alkenyl and aryl and one or more of the carbon atoms in the alkyl, alkenyl and cycloalkyl groups may be optionally replaced with a heteromoiety selected from O, S, N, NH and $NC_{1-4}$alkyl.

Reduction of compounds of Formula (XI) using a compound of the disclosure according to the process described above provides the corresponding hydrogenated compounds of Formula (XII):




(XII)

wherein Z, $R^{22}$ and $R^{23}$ are defined as in Formula (XII).

Since $R^{22}$ and $R^{23}$ may be different, it is hereby understood that the final product of Formula (XII), may be chiral, thus possibly consisting of a practically pure enantiomer or of a mixture of stereoisomers, depending on the nature of the catalyst used in the process.

In an embodiment of the disclosure, the hydrogenation conditions characterizing the above process may comprise a base. Said base can be the substrate itself, if the latter is basic, or any conventional base. One can cite, as non-limiting examples, organic non-coordinating bases such as DBU, an alkaline or alkaline-earth

metal carbonate, a carboxylate salt such as sodium or potassium acetate, or an alcoholate or hydroxide salt. In an embodiment of the disclosure, the bases are the alcoholate or hydroxide salts selected from the group consisting of the compounds of formula $(R^{30}O)_2M'$ and $R^{30}OM''$, wherein M' is an alkaline-earth metal, M'' is an alkaline metal and $R^{30}$ stands for hydrogen or a linear or branched $C_{1-20}$alkyl group.

Standard hydrogenation conditions, as used herein, typically implies the mixture of the substrate with a metal complex of Formula (I), (II), (III), (IV) or (V) with or without a base, possibly in the presence of a solvent, and then treating such a mixture with a hydrogen donor solvent at a chosen pressure and temperature (transfer hydrogenation) or in an atmosphere of hydrogen gas at a chosen pressure and temperature. Varying the reaction conditions, including for example, temperature, pressure, solvent and reagent ratios, to optimize the yield of the desired product would be well within the abilities of a person skilled in the art.

The following non-limiting examples are illustrative of the present disclosure:

EXAMPLES

The disclosure will now be described in further details by way of the following examples, wherein the temperatures are indicated in degrees centigrade and the abbreviations have the usual meaning in the art. All the procedures described hereafter have been carried out under an inert atmosphere unless stated otherwise. All preparations and manipulations were carried out under $H_2$, $N_2$ or Ar atmospheres with the use of standard Schlenk, vacuum line and glove box techniques in dry, oxygen-free solvents. Tetrahydrofuran (THF), diethyl ether ($Et_2O$), methylene chloride and hexanes were obtained using an IT solvent purification system. Deuterated solvents were degassed and dried over activated molecular sieves. NMR spectra were recorded on a 300 MHz spectrometer (300 MHz for $^1H$, 75 MHz for $^{13}C$ and 121.5 for $^{31}P$). All $^{31}P$ chemical shifts were measured relative to 85% $H_3PO_4$ as an external reference. $^1H$ and $^{13}C$ chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane.

*Example 1: Synthesis of Cationic Ruthenium Precursors.*

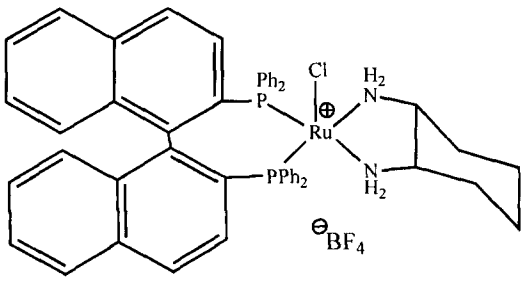
*(a) $[RuCl(p\text{-cymene})]_2[BF_4]_2$*

In an Ar filled flask, 0.25 g (0.041 mmol) $[RuCl_2(p\text{-cymene})]_2$ and 0.16 g (0.082 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (10 mL) was added and the resulting orange suspension was left to stir at ambient temperature. Within several minutes the suspension darkened to brown/green in colour. After 2 hours, the suspension was filtered through Celite and the orange filtrate was reduced to approximately 1 mL in volume. Addition of hexane afforded an oily orange solid which was washed repeatedly with hexane and dried in vacuo. Yield: 0.215 g (74 %).

*Example 2: Synthesis of Cationic Ruthenium Hydrogenation Catalysts*

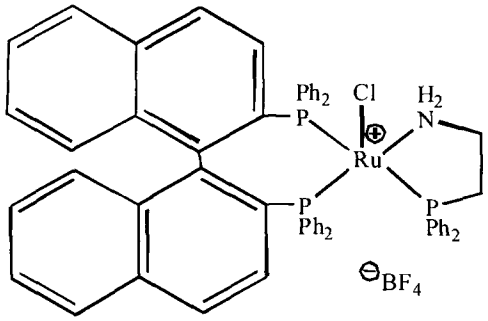
*(a) [RuCl(R-binap)(R,R-cydn)]$BF_4$*

In an Ar filled flask, 0.600 g (0.66 mmol) of $RuCl_2$(R-binap)(R,R-cydn) and 0.129 g (0.66 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (15 mL) was added and the resulting rust coloured suspension was left to stir at ambient temperature for two hours after which time it was filtered, in air, through Celite. The orange filtrate was reduced to dryness leaving an orange residue. Yield: 0.620 g (97 %). $^{31}P$ NMR (ppm, $CDCl_3$): 7.53 (d, $J_{PP}$ = 45 Hz), 67.5 (d, $J_{PP}$ = 45 Hz).



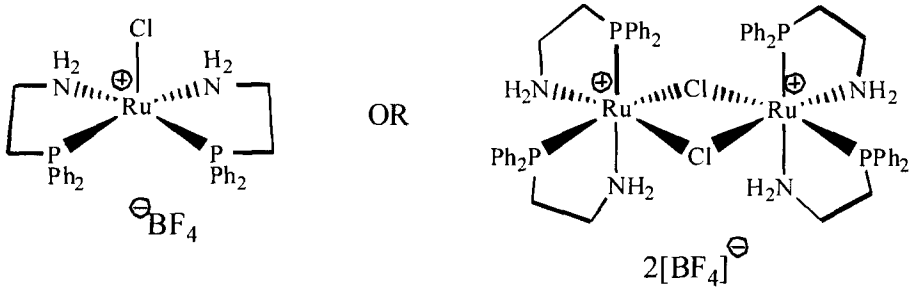

*(b) [RuCl(R-binap)($Ph_2PCH_2CH_2NH_2$)]$BF_4$*

In an Ar filled flask, 0.766 g (0.73 mmol) of $RuCl_2$(R-binap)($Ph_2PCH_2CH_2NH_2$) and 0.143 g (0.73 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (15 mL) was added and the resulting dark orange suspension was left to stir at ambient temperature for two hours after which time it was filtered, in air, through Celite. The dark orange filtrate was reduced to dryness leaving a deep orange residue. Yield: 0.790 g (98 %). $^{31}P$ NMR (ppm, $CDCl_3$): 32.6 (dd, $J_{PP}$ = 31 Hz, $J_{PP}$ = 24 Hz), 48.0 (dd, $J_{PP}$ = 34 Hz, $J_{PP}$ = 31 Hz), 62.7 (dd, $J_{PP}$ = 34 Hz, $J_{PP}$ = 24 Hz).




*(c) [RuCl(Ph$_2$PCH$_2$CH$_2$NH$_2$)$_2$]BF$_4$*

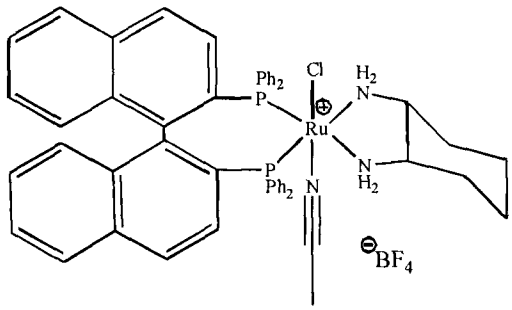
In an Ar filled flask, 0.750 g (1.19 mmol) of $RuCl_2(Ph_2PCH_2CH_2NH_2)_2$ and 0.232 g (1.19 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (15 mL) was added and the resulting red suspension was left to stir at ambient temperature for two hours after which time it was filtered, in air, through Celite. The dark red filtrate was reduced to dryness leaving a deep red residue. Yield: 0.790 g (97 %). $^{31}P$ NMR (ppm, acetone-$D_6$): 55.0 (d, $J_{PP}$ = 36 Hz), 73.3 (d, $J_{PP}$ = 36 Hz).




*(d) [RuCl(MeCN)(R-binap)(R,R-cydn)]BF$_4$*

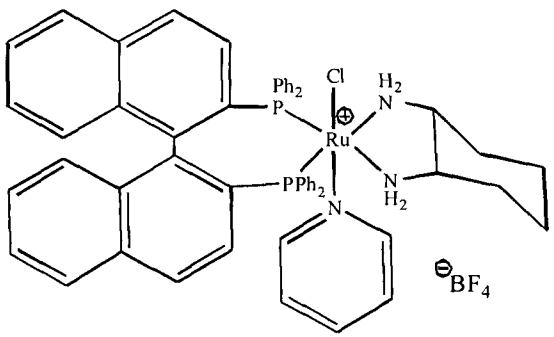
In an Ar filled flask, 0.150 g (0.16 mmol) of [RuCl(R-binap)(R,R-cydn)]$BF_4$ was dissolved in 6 mL of $CH_2Cl_2$ and 41 mL (0.78 mmol) of MeCN was added and the brown solution was left to stir. After 16 hours the solution had changed to pale green in colour. Removal of an aliquot for subsequent $^{31}P$ NMR analysis showed that no starting material remained. Concentration of the solvent to approximately 1 mL followed by the addition of hexane (10 mL) afforded a pale green solid. The solid was filtered off, washed with hexane (2 × 5 mL) and dried in vacuo. Yield: 0.127 g (81 %). NMR analysis of the isolated solid revealed the

presence of several isomeric species, the major constituent accounting for 80 % of the integrated intensity. NMR data are given only for the major isomer. $^{31}P$ NMR (ppm, $CDCl_3$): 46.3 (d, $J_{PP}$ = 34 Hz), 48.8 (d, $J_{PP}$ = 34 Hz).



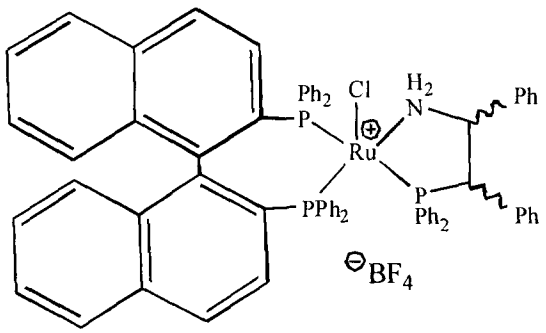

*(e) [RuCl(pyridine)(R-binap)(R,R-cydn)]$BF_4$*

In an Ar filled flask, 0.150 g (0.16 mmol) of [RuCl(R-binap)(R,R-cydn)]$BF_4$ was dissolved in 6 mL of $CH_2Cl_2$ and 63 mL (0.78 mmol) of pyridine was added and the brown solution was left to stir. After 16 hours the solution had changed to yellow in colour. Removal of an aliquot for subsequent $^{31}P$ NMR analysis showed that no starting material remained. Concentration of the solvent to approximately 1 mL followed by the addition of hexane (10 mL) afforded a yellow solid. The solid was filtered off, washed with hexane (2 × 5 mL) and dried in vacuo Yield: 0.152 g (94 %). NMR analysis of the isolated solid revealed two complexes; one identified as the desired product (NMR data given below) and the other as starting material (see above). The two compounds were present in approximately equal amounts. It is unclear if a single product is isolated and dissociation of bound pyridine occurs upon dissolution or if reversion to starting material occurs during isolation. $^{31}P$ NMR (ppm, $CDCl_3$): 55.2 (d, $J_{PP}$ = 37 Hz), 49.4 (d, $J_{PP}$ = 37 Hz).



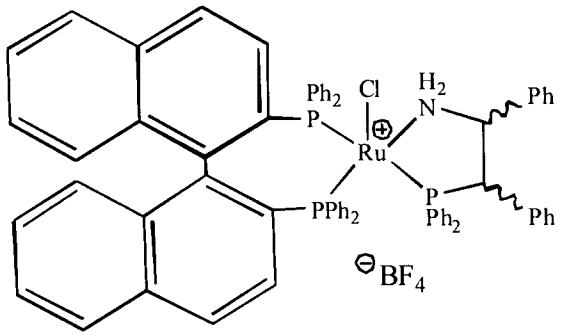

*(f) [RuCl(R-binap)(S,S-$Ph_2PCH(Ph)CH(Ph)NH_2$)]$BF_4$*

In an Ar filled flask, 0.150 g (0.13 mmol) of $RuCl_2$(R-binap)(S,S-$Ph_2PCH(Ph)CH(Ph)NH_2$) and 0.025 g (0.13 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (6 mL) was added and the resulting green suspension was left to stir at ambient temperature for sixteen hours over which time it changed to brown in colour. The suspension was filtered, in air, through Celite and the brown filtrate was reduced to dryness leaving a brown residue. Yield: 0.108 g (69 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 34.5 (pseudo t, $J_{PP}$ = 27 Hz), 44.5 (dd, $J_{PP}$ = 31 Hz, $J_{PP}$ = 28 Hz), 83.9 (dd, $J_{PP}$ = 31 Hz, $J_{PP}$ = 26 Hz).



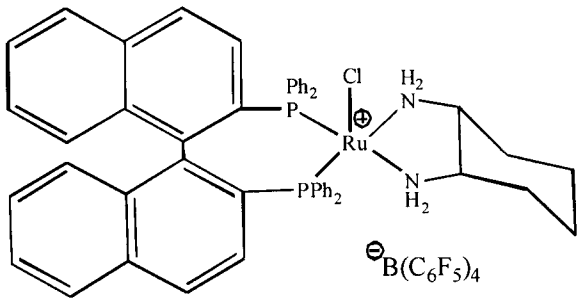

*(g) [RuCl(S-binap)(S,S-$Ph_2PCH(Ph)CH(Ph)NH_2$)]$BF_4$*

In an Ar filled flask, 0.150 g (0.13 mmol) of $RuCl_2$(S-binap)(S,S-$Ph_2PCH(Ph)CH(Ph)NH_2$) and 0.025 g (0.13 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (6 mL) was added and the resulting green suspension was left to stir at ambient temperature for sixteen hours over which time it changed to brown in colour. The suspension was filtered, in air, through Celite and the brown filtrate was reduced to dryness leaving a brown residue. Yield: 0.096 g (61 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 26.7 (dd, $J_{PP}$ = 27 Hz, $J_{PP}$ = 20 Hz), 48.5 (dd, $J_{PP}$ = 33 Hz, $J_{PP}$ = 27 Hz), 86.3 (dd, $J_{PP}$ = 33 Hz, $J_{PP}$ = 20 Hz).



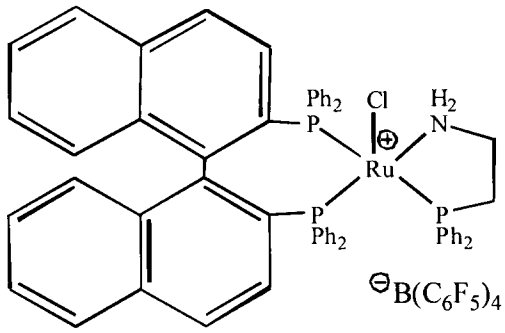

*(h) [RuCl(R-binap)(R,R-cydn)][B($C_6F_5$)$_4$]*

In an Ar filled flask, 0.200 g (0.22 mmol) of $RuCl_2$(R-binap)(R,R-cydn) and 0.192 g (0.22 mmol) of [Li($OEt_2$)$_{2.5}$][B($C_6F_5$)$_4$] were combined. $CH_2Cl_2$ (10 mL) was added and the resulting dark orange suspension was left to stir at ambient temperature for 16 hours after which time it was filtered, in air, through Celite. The orange filtrate was reduced to dryness leaving an orange residue. Yield: 0.247 g (72 %). $^{31}$P NMR (ppm, $CDCl_3$): 13.1 (d, $J_{PP}$ = 46 Hz), 72.6 (d, $J_{PP}$ = 46 Hz).



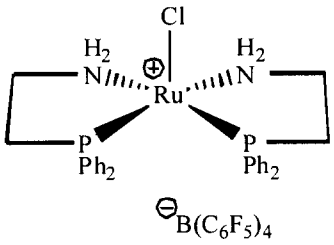

*(i) [RuCl(R-binap)($Ph_2PCH_2CH_2NH_2$)][B($C_6F_5$)$_4$]*

In an Ar filled flask, 0.200 g (0.20 mmol) of $RuCl_2$(R-binap)($Ph_2PCH_2CH_2NH_2$) and 0.170 g (0.20 mmol) of [Li($OEt_2$)$_{2.5}$][B($C_6F_5$)$_4$] were combined. $CH_2Cl_2$ (10 mL) was added and the resulting dark orange suspension was left to stir at ambient temperature for sixteen hours after which time it was filtered, in air, through Celite. The dark orange filtrate was reduced to dryness leaving a deep orange residue. Yield: 0.273 g (84 %). $^{31}$P NMR (ppm, $CD_2Cl_2$): 31.3 (dd, $J_{PP}$ = 31 Hz, $J_{PP}$ = 24 Hz), 48.0 (dd, $J_{PP}$ = 35 Hz, $J_{PP}$ = 31 Hz), 62.2 (dd, $J_{PP}$ = 35 Hz, $J_{PP}$ = 24 Hz).

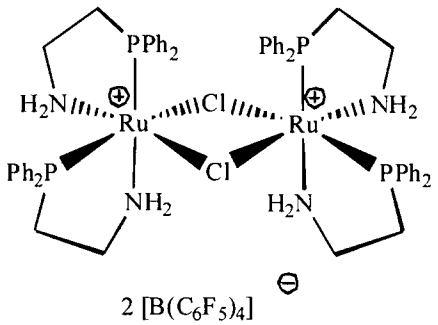



*(j) [RuCl(Ph$_2$PCH$_2$CH$_2$NH$_2$)$_2$][B(C$_6$F$_5$)$_4$]*

In an Ar filled flask, 0.200 g (0.32 mmol) of $RuCl_2(Ph_2PCH_2CH_2NH_2)_2$ and 0.276 g (0.32 mmol) of $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ were combined. $CH_2Cl_2$ (10 mL) was added and the resulting orange suspension was left to stir at ambient temperature for sixteen hours after which time it was filtered, in air, through Celite. The orange filtrate was reduced to dryness leaving a deep orange residue. Yield: 0.273 g (86 %). $^{31}P$ NMR (ppm, acetone-$D_6$): 54.9 (d, $J_{PP}$ = 36 Hz), 72.7 (d, $J_{PP}$ = 36 Hz).



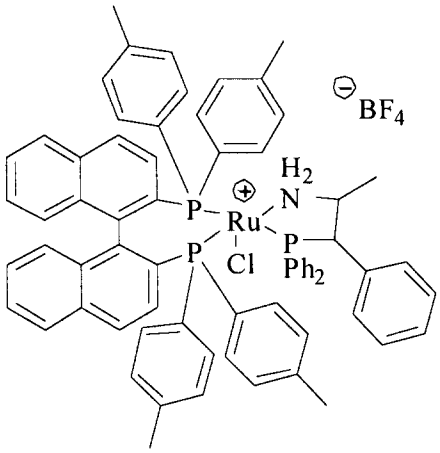

OR




*(k) [RuCl(R-tolbinap)(R,R-Ph$_2$PCH(Ph)CH(CH$_3$)NH$_2$)]BF$_4$*

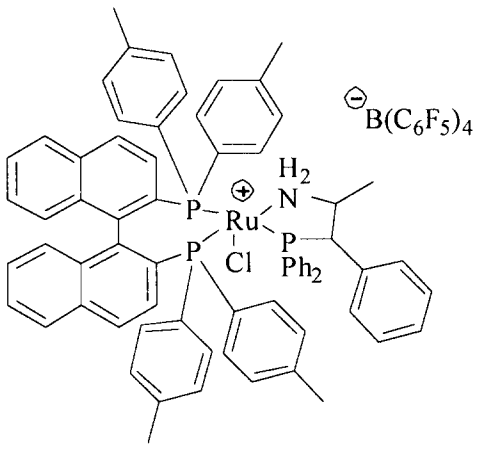
In an Ar filled flask, 0.150 g (0.13 mmol) of $RuCl_2$(R-tolbinap)(R,R-$Ph_2PCH(Ph)CH(Me)NH_2$) and 0.025 g (0.13 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (10 mL) was added and the resulting brown suspension was left to stir at ambient temperature for 2 hours. The suspension was then filtered, in air, through Celite and the brown filtrate was reduced to dryness leaving a brown residue. Yield:

0.112 g (72 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 25.3 (br m), 48.6 (br t, $J_{PP}$ = 30 Hz), 87.6 (dd, $J_{PP}$ = 30 Hz, $J_{PP}$ = 20 Hz).



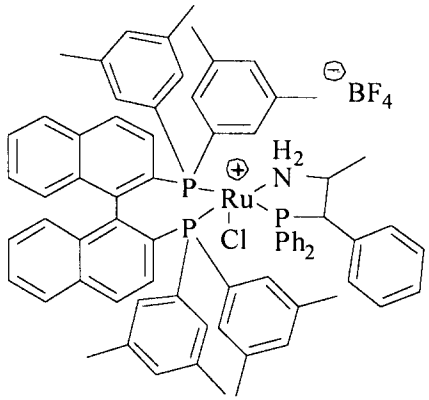

*(l) [RuCl(R-tolbinap)(R,R-$Ph_2PCH(Ph)CH(CH_3)NH_2$)][$B(C_6F_5)_4$]*

In an Ar filled flask, 0.100 g (0.085 mmol) of $RuCl_2$(R-tolbinap)(R,R-$Ph_2PCH(Ph)CH(Me)NH_2$) and 0.074 g (0.085 mmol) of $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ were combined. $CH_2Cl_2$ (10 mL) was added and the resulting brown suspension was left to stir at ambient temperature for 2 hours. The suspension was then filtered, in air, through Celite and the brown filtrate was reduced to dryness leaving a brown residue. Yield: 0.123 g (79 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 25.3 (br m), 48.4 (br t, $J_{PP}$ = 30 Hz), 87.7 (dd, $J_{PP}$ = 30 Hz, $J_{PP}$ = 20 Hz).



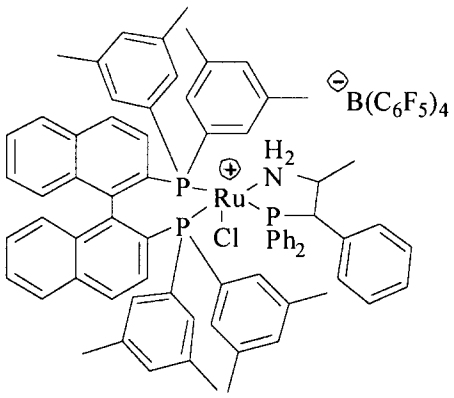
*(m) [RuCl(R-3,5-xylylbinap)(R,R-$Ph_2PCH(Ph)CH(CH_3)NH_2$)]$BF_4$*

$^{31}P$ NMR (ppm, $CD_2Cl_2$): 31.6 (br m), 46.3 (br t, $J_{PP}$ = 32 Hz), 89.4 (br m).



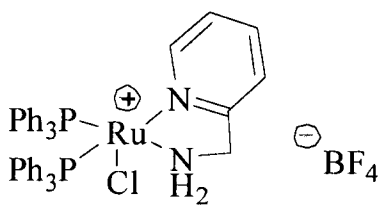
*(n) [RuCl(R-3,5-xylylbinap)(R,R-$Ph_2PCH(Ph)CH(CH_3)NH_2$)][$B(C_6F_5)_4$]*

$^{31}P$ NMR (ppm, $CD_2Cl_2$): 31.6 (br m), 46.3 (br m), 89.4 (dd, $J_{PP}$ = 33 Hz, $J_{PP}$ = 28 Hz).



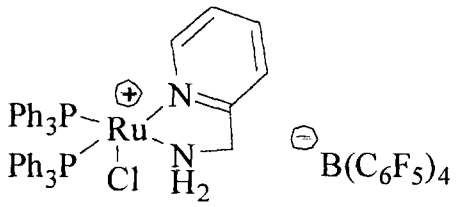
*(o) [$RuCl(NH_2CH_2Py)(PPh_3)_2$]$BF_4$*

$^{31}P$ NMR (ppm, $CD_2Cl_2$): 14.2 (br), 38.4 (br m), 56.6 (br m).



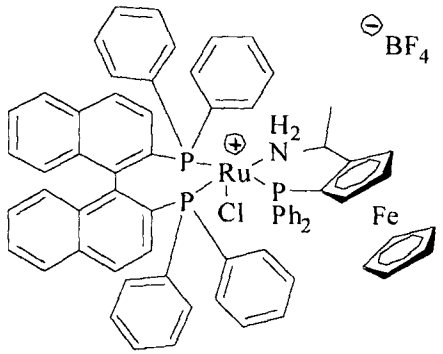
*(p) [RuCl(NH$_2$CH$_2$Py)(PPh$_3$)$_2$][B(C$_6$F$_5$)$_4$]*

$^{31}$P NMR (ppm, $CD_2Cl_2$): 38.8 (d, $J_{PP}$ = 27 Hz), 41.0 (br), 55.4 (d, $J_{PP}$ = 27 Hz).



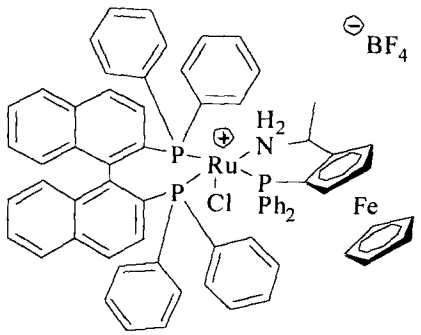
*(q) [RuCl(R-binap)(S$_C$, R$_P$-(NH$_2$CH(CH$_3$)-Fc-PPh$_2$))]BF$_4$*

$^{31}$P NMR (ppm, $CD_2Cl_2$): 42.4 (br m), 54.5 (br).



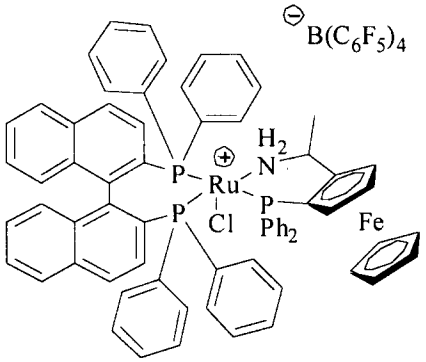
*(r) [RuCl(R-binap)(R$_C$, S$_P$-(NH$_2$CH(CH$_3$)-Fc-PPh$_2$))]BF$_4$*

$^{31}$P NMR (ppm, $CD_2Cl_2$): No resolved peaks at ambient temperature.



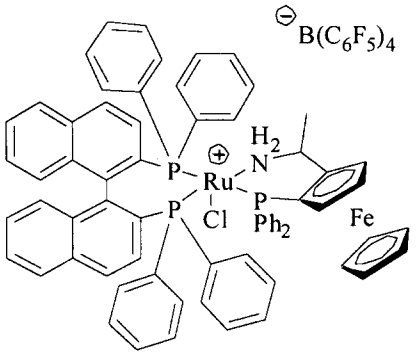
*(s) [RuCl(R-binap)($S_C$, $R_P$-($NH_2CH(CH_3)$-Fc-$PPh_2$))][$B(C_6F_5)_4$]*

$^{31}$P NMR (ppm, $CD_2Cl_2$): 42.7 (br m), 55.1 (br m).



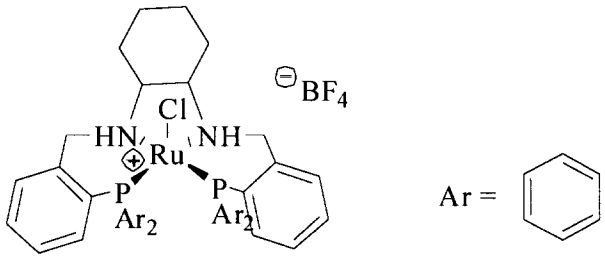

*(t) [RuCl(R-binap)($R_C$, $S_P$-($NH_2CH(CH_3)$-Fc-$PPh_2$))][$B(C_6F_5)_4$]*

$^{31}$P NMR (ppm, $CD_2Cl_2$): 44.0 (br), 68.0 (br).



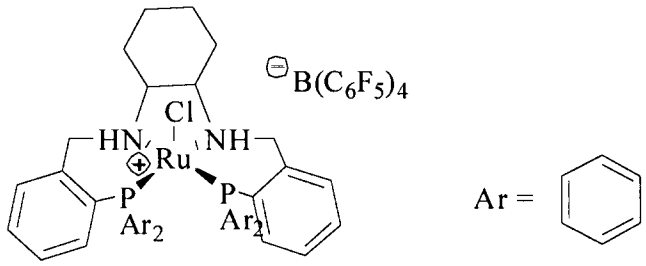

*(u) [RuCl(R,R-DPPcydn)]$BF_4$*

$^{31}$P NMR (ppm, $CD_2Cl_2$): Several broadened peaks between 10 and 70 ppm.



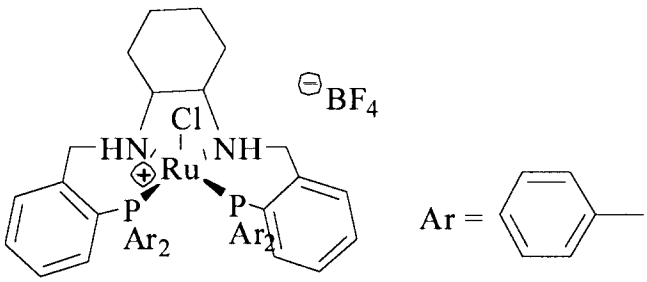
*(v) [RuCl(R,R-DPPcydn)][B($C_6F_5$)$_4$]*

$^{31}$P NMR (ppm, $CD_2Cl_2$): Several broadened peaks between 10 and 70 ppm.



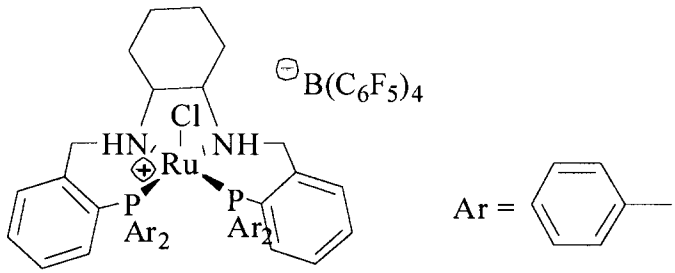

*(w) [RuCl(R,R-di(p-tolyl)PPcydn)]$BF_4$*

$^{31}$P NMR (ppm, $CD_2Cl_2$): Several broadened peaks between 10 and 70 ppm.



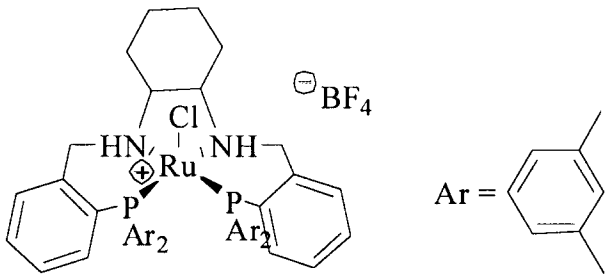

*(x) [RuCl(R,R-di(p-tolyl)PPcydn)][B($C_6F_5$)$_4$]*

$^{31}$P NMR (ppm, $CD_2Cl_2$): Several broadened peaks between 10 and 70 ppm.



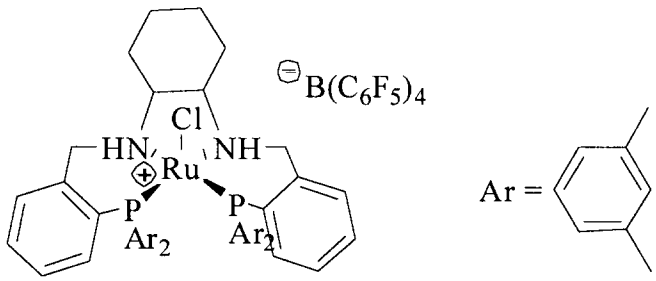

*(y) [RuCl(R,R-di(3,5-xylyl)PPcydn)]$BF_4$*

$^{31}$P NMR (ppm, $CD_2Cl_2$): Several broadened peaks between 10 and 70 ppm.



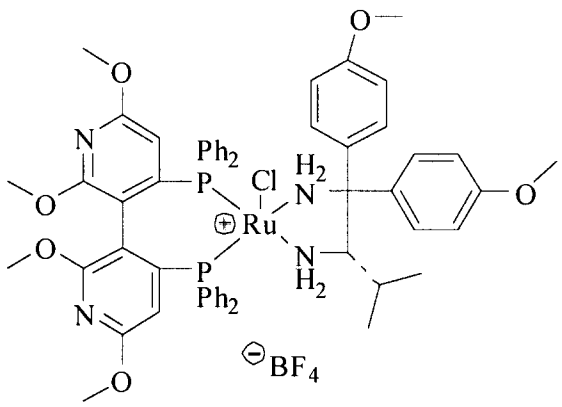

*(z) [RuCl(R,R-di(3,5-xylyl)PPcydn)][B($C_6F_5$)$_4$]*

$^{31}$P NMR (ppm, $CD_2Cl_2$): Several broadened peaks between 10 and 70 ppm.



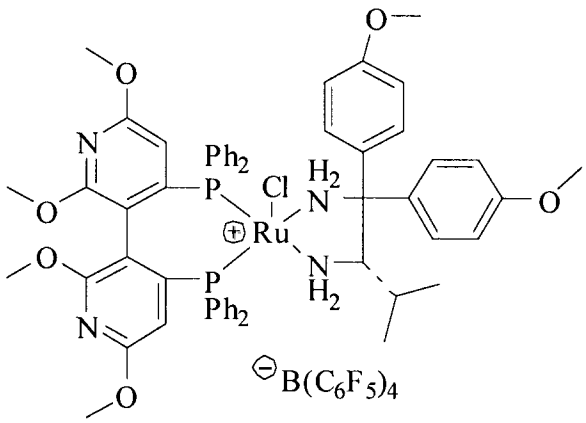

*(aa) [RuCl(S-PPhos)(S-DAIPEN)]$BF_4$*

$^{31}$P NMR (ppm, $CD_2Cl_2$): Several broadened peaks between 40 and 65 ppm.



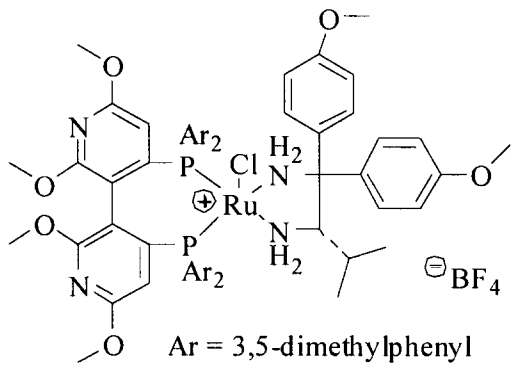

*(bb) [RuCl(S-PPhos)(S-DAIPEN)][B($C_6F_5$)$_4$]*

$^{31}$P NMR (ppm, $CD_2Cl_2$): Several broadened peaks between 40 and 75 ppm.



*(cc) [RuCl(S-XylylPPhos)(S-DAIPEN)]BF$_4$*

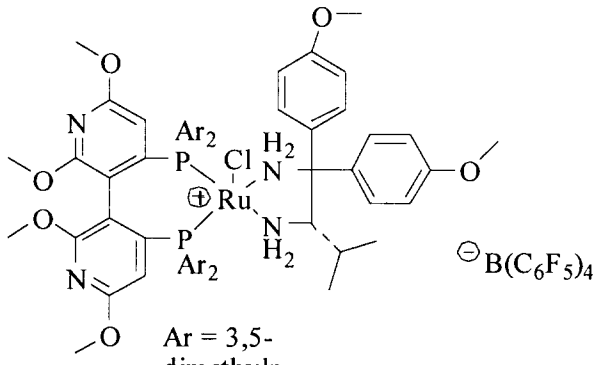
$^{31}$P NMR (ppm, $CD_2Cl_2$): Several broadened peaks between 40 and 65 ppm.



Ar = 3,5-dimethylphenyl

*(dd) [RuCl(S-XylylPPhos)(S-DAIPEN)][B(C$_6$F$_5$)$_4$]*

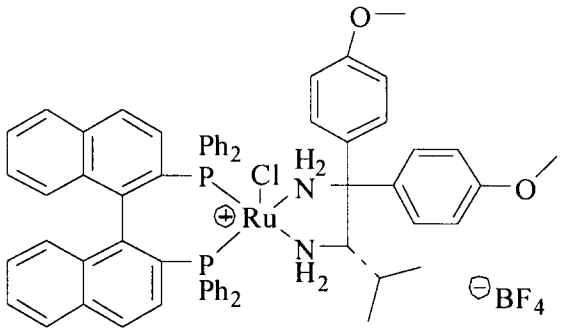
$^{31}$P NMR (ppm, $CD_2Cl_2$): Several broadened peaks between 40 and 75 ppm.



Ar = 3,5-dimethylphenyl

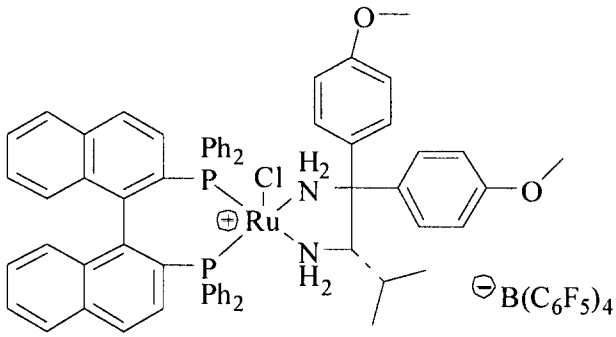
*(ee) [RuCl(S-binap)(S-DAIPEN)]$BF_4$*

$^{31}P$ NMR (ppm, $CD_2Cl_2$): Several broadened peaks between 40 and 65 ppm.

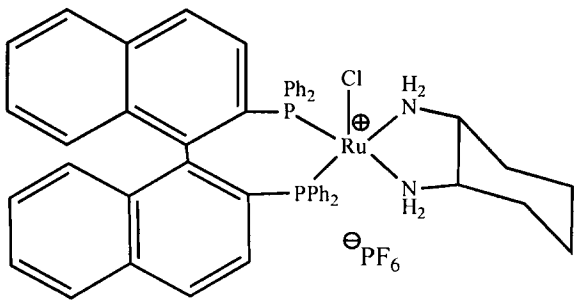



*(ff) [RuCl(S-binap)(S-DAIPEN)][$B(C_6F_5)_4$]*

$^{31}P$ NMR (ppm, $CD_2Cl_2$): Several broadened peaks between -20 and 70 ppm.



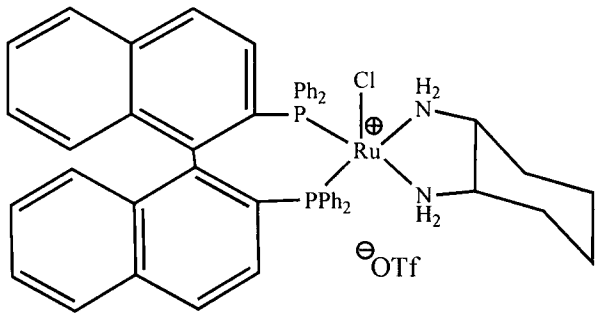

*(gg) [(R-binap)RuCl(R,R-dach)]$PF_6$.*




In an Ar filled flask, 0.280 g (0.31 mmol) of $RuCl_2$(*R*-binap)(*R,R*-dach) and 0.078 g (0.31 mmol) of $AgPF_6$ were combined. $CH_2Cl_2$ (15 mL) was added and the resulting brown coloured suspension was left to stir at ambient temperature

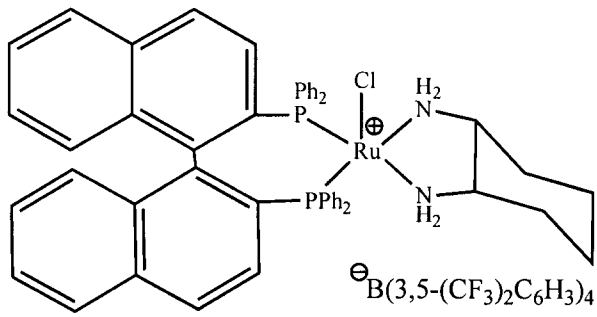
for 24 hours after which time it was filtered, in air, through a 0.45 mm PTFE syringe filter. The orange filtrate was reduced to dryness leaving an orange residue. Yield: 0.280 g (89 %). $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): 7.53 (d, $^{2}J_{PP}$ = 45 Hz), 67.5 (d, $^{2}J_{PP}$ = 45 Hz), 208.6 (septuplet, $^{2}J_{PF}$ = 710 Hz). ***R,R*-dach = *R,R*-cydn

*(hh) [(R-binap)RuCl(R,R-dach)]OTf.*




In an Ar filled flask, 0.100 g (0.11 mmol) of $RuCl_2$(*R*-binap)(*R,R*-dach) and 0.028 g (0.11 mmol) of AgOTf were combined. $CH_2Cl_2$ (5 mL) was added and the resulting rust coloured suspension was left to stir at ambient temperature for 2 hours after which time it was filtered, in air, through a 0.45 mm PTFE syringe filter. The orange filtrate was reduced to dryness leaving an orange residue. Yield: 0.065 g (58 %). $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): 7.53 (d, $^{2}J_{PP}$ = 45 Hz), 67.5 (d, $^{2}J_{PP}$ = 45 Hz). ). ***R,R*-dach = *R,R*-cydn

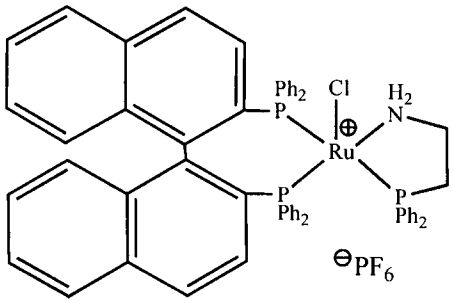
*(ii) [(R-binap)RuCl(R,R-dach)][B(3,5-(CF3)2C6H3)4].*




In an Ar filled flask, 0.100 g (0.11 mmol) of $RuCl_2$(*R*-binap)(*R,R*-dach), 0.097 g (0.11 mmol) of $Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ and 21 mg (0.11 mmol) of $AgBF_4$ were combined. $CDCl_3$ (2 mL) was added and the resulting rust coloured suspension was left to stir at ambient temperature for 18 hours after which time it was filtered, in air, through a 0.45 mm PTFE syringe filter. The orange filtrate was reduced to dryness leaving a yellow-orange residue. Yield: 0.115 g (61 %). $^{31}P\{^{1}H\}$

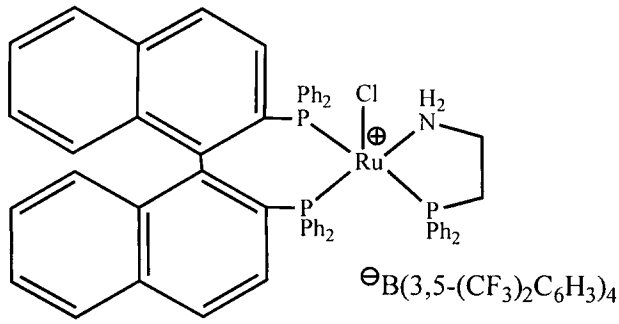
NMR (ppm, $CDCl_3$): 7.73 (d, $^2J_{PP}$ = 45 Hz), 67.2 (d, $^2J_{PP}$ = 45 Hz)). **$R,R$-dach = $R,R$-cydn

*(jj) [(R-binap)RuCl(PGly)]$PF_6$*




In an Ar filled flask, 0.075 g (0.074 mmol) of $RuCl_2$(*R*-binap)($Ph_2PCH_2CH_2NH_2$) and 0.019 g (0.074 mmol) of $AgPF_6$ were combined. $CH_2Cl_2$ (5 mL) was added and the resulting dark orange suspension was left to stir at ambient temperature for 24 hours after which time it was filtered, in air, through a 0.45 mm PTFE syringe filter. The dark brown-orange filtrate was reduced to dryness leaving a brown residue. Yield: 0.032 g (39 %). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): 32.6 (dd, $^2J_{PP}$ = 31 Hz, $^2J_{PP}$ = 24 Hz), 48.0 (dd, $^2J_{PP}$ = 34 Hz, $^2J_{PP}$ = 31 Hz), 62.7 (dd, $^2J_{PP}$ = 34 Hz, $^2J_{PP}$ = 24 Hz). There is also formation of another unidentified AB signal in $^{31}P$ NMR: 15.3 (d, $^2J_{PP}$ = 17 Hz), 17.3 (d, $^2J_{PP}$ = 17 Hz). **PGly = $Ph_2PCH_2CH_2NH_2$

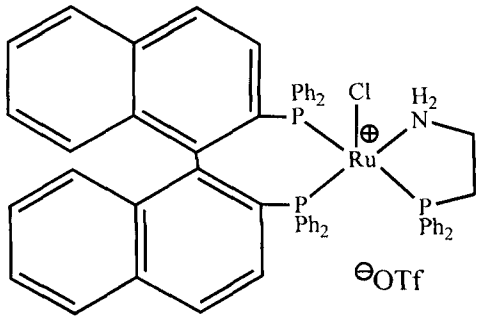
*(kk) [(R-binap)RuCl(PGly)][B(3,5-$(CF_3)_2C_6H_3)_4$]*




In an Ar filled flask, 0.08 g (0.078 mmol) of $RuCl_2$(*R*-binap)($Ph_2PCH_2CH_2NH_2$), 0.069 g (0.078 mmol) of Na[B(3,5-$(CF_3)_2C_6H_3)_4$] and 15 mg (0.078 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (2 mL) was added and the resulting rust coloured suspension was left to stir at ambient temperature for 18 hours after which time it was filtered, in air, through a 0.45 mm PTFE syringe filter. The orange filtrate was reduced to dryness leaving a yellow-orange residue. Yield: 0.090 g

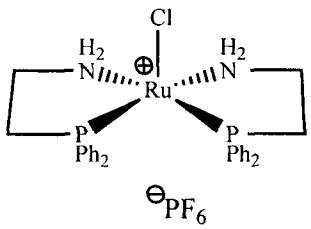
(63 %). $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): 7.73 (d, $^{2}J_{PP}$ = 45 Hz), 67.2 (d, $^{2}J_{PP}$ = 45 Hz). **PGly = $Ph_2PCH_2CH_2NH_2$

*(ll) [(R-binap)RuCl(PGly)]OTf*

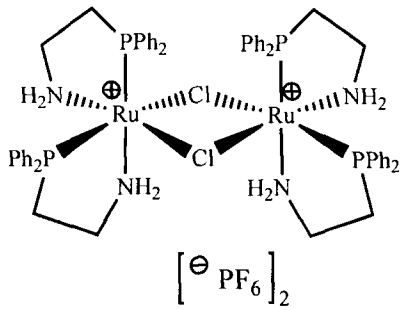



In an Ar filled flask, 0.150 g (0.15 mmol) of $RuCl_2$(*R*-binap)(PGly) and 0.038 g (0.15 mmol) of AgOTf were combined. $CH_2Cl_2$ (5 mL) was added and the resulting dark brown suspension was left to stir at ambient temperature for 24 hours after which time it was filtered, in air, through a 0.45 mm PTFE syringe filter. The dark brown filtrate was reduced to dryness leaving a brown-yellow residue. Yield: 0.130 g (78 %). $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): 29.4 (t, $^{2}J_{PP}$ = 27 Hz), 45.8 (dd, $^{2}J_{PP}$ = 33 Hz), 60.5 (t, $^{2}J_{PP}$ = 27 Hz). There is also formation of another unidentified AB signal in $^{31}P$ NMR: 13.4 (d, $^{2}J_{PP}$ = 17 Hz), 15.4 (d, $^{2}J_{PP}$ = 17 Hz). **PGly = $Ph_2PCH_2CH_2NH_2$

*(mm) [RuCl(PGly)$_2$]PF$_6$*

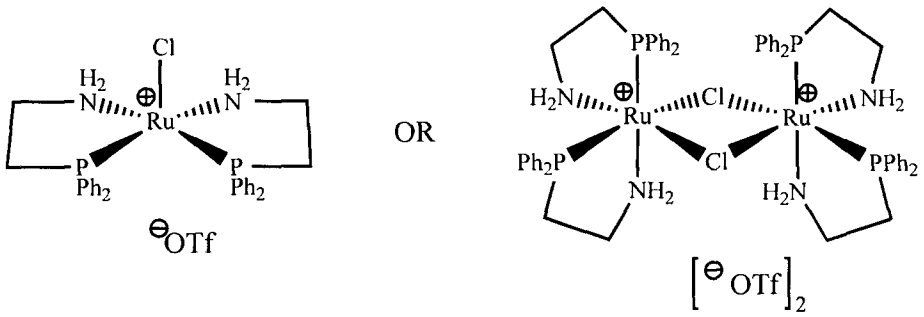



OR



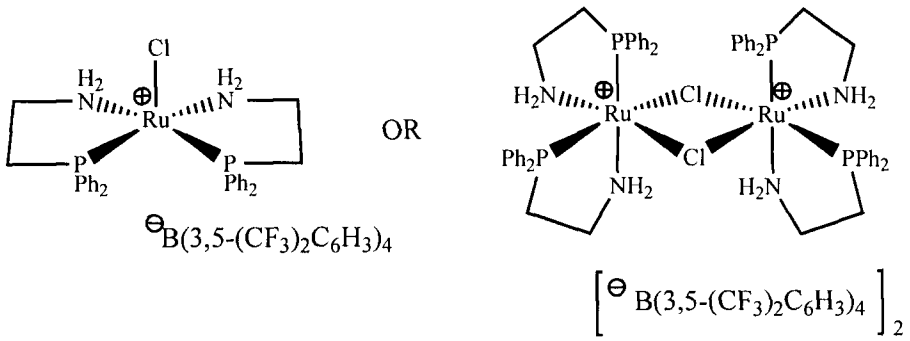

In an Ar filled flask, 0.075 g (0.12 mmol) of $RuCl_2(PGly)_2$ and 0.030 g (0.12 mmol) of $AgPF_6$ were combined. $CH_2Cl_2$ (5 mL) was added and the resulting brown suspension was left to stir at ambient temperature for 24 hours after which time it was filtered, in air, through a 0.45 mm PTFE syringe filter. The dark orange filtrate was reduced to dryness leaving a yellow brown residue. Yield: 0.030 g (35 %). $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$): 7 different doublets in the range 52-73 ppm. **PGly = $Ph_2PCH_2CH_2NH_2$

*(nn) [RuCl(PGly)$_2$]OTf*



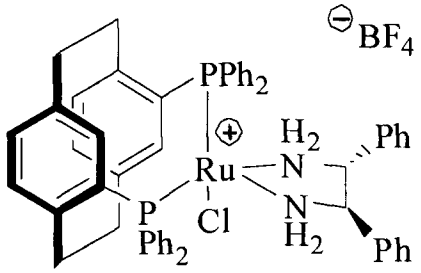

In an Ar filled flask, 0.150 g (0.24 mmol) of $RuCl_2(PGly)_2$ and 0.061 g (0.24 mmol) of $AgPF_6$ were combined. $CH_2Cl_2$ (10 mL) was added and the resulting brown suspension was left to stir at ambient temperature for 24 hours after which time it was filtered, in air, through a 0.45 mm PTFE syringe filter. The dark yellow brown filtrate was reduced to dryness leaving an orange residue. Yield: 0.095 g (53 %). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): 7 different doublets in the range 52-73 ppm. **PGly = $Ph_2PCH_2CH_2NH_2$

*(oo) [RuCl(PGly)$_2$][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]*



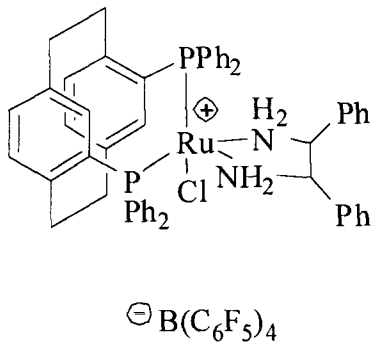

In an Ar filled flask, 0.08 g (0.13 mmol) of $RuCl_2(PGly)_2$, 0.112 g (0.13 mmol) of $Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ and 25 mg (0.13 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (2 mL) was added and the resulting rust coloured suspension was left to stir at ambient temperature for 18 hours after which time it was filtered, in air, through a 0.45 mm PTFE syringe filter. The orange filtrate was reduced to dryness leaving an orange residue. Yield: 0.030 g (16 %). 6 different doublets in the range 30-51 ppm. **PGly = $Ph_2PCH_2CH_2NH_2$

*(pp) [RuCl(S-PhanePhos)(R,R-DPEN)]BF$_4$*



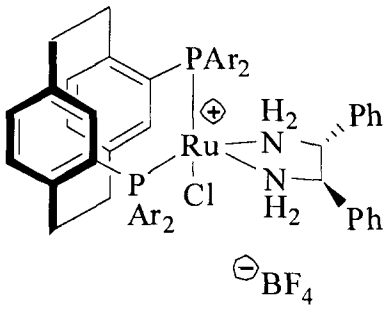
In an Ar filled flask, 0.100 g (0.10 mmol) of $RuCl_2$(*S*-PhanePhos)(*R,R*-DPEN) and 0.020 g (0.10 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (5 mL) was added and the resulting brown suspension was left to stir at ambient temperature for sixteen hours. The suspension was filtered, in air, through Celite and the brown filtrate was reduced to dryness leaving a brown residue. Yield: 0.048 g (46 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 52.0 (d, $J_{PP}$ = 28 Hz), 43.1 (d, $J_{PP}$ = 28 Hz).

*(qq) [RuCl(S-PhanePhos)(R,R-DPEN)]B(C$_6$F$_5$)$_4$*



In an Ar filled flask, 0.050 g (0.06 mmol) of $RuCl_2$(*S*-PhanePhos)(*R,R*-DPEN) and 0.045 g (0.06 mmol) of $Li(OEt_2)_{2.5}[B(C_6F_5)_4]$ were combined. $CH_2Cl_2$ (5 mL) was added and the resulting brown suspension was left to stir at ambient temperature for sixteen hours. The suspension was filtered, in air, through Celite and the brown filtrate was reduced to dryness leaving a brown residue. Yield: 0.036 g (40 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 50.5 (d, $J_{PP}$ = 28 Hz), 42.4 (d, $J_{PP}$ = 28 Hz).

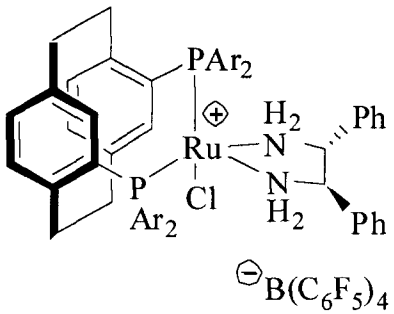
*(rr) [RuCl(S-XylylPhanePhos)(R,R-DPEN)]BF$_4$*



Ar = 3,5-dimethylphenyl

In an Ar filled flask, 0.100 g (0.10 mmol) of $RuCl_2$(*S*-XylylPhanePhos)(*R,R*-DPEN) and 0.018 g (0.10 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (5 mL) was added and the resulting brown suspension was left to stir at ambient temperature for sixteen hours. The suspension was filtered, in air, through Celite and the brown filtrate was reduced to dryness leaving a brown residue. Yield: 0.066 g (63 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 52 (d, $J_{PP}$ = 28 Hz), 42 (d, $J_{PP}$ = 28 Hz).

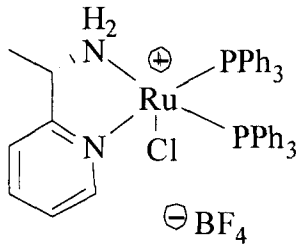
*(ss) [RuCl(S-XylylPhanePhos)(R,R-DPEN)]B($C_6F_5$)$_4$*




Ar = 3,5-dimethylphenyl

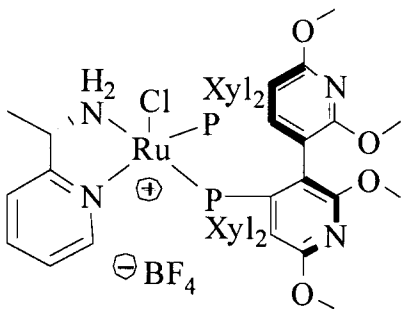
In an Ar filled flask, 0.050 g (0.05 mmol) of $RuCl_2$(*S*-PhanePhos)(*R,R*-DPEN) and 0.041 g (0.05 mmol) of $Li(OEt_2)_{2.5}[B(C_6F_5)_4]$ were combined. $CH_2Cl_2$ (5 mL) was added and the resulting brown suspension was left to stir at ambient temperature for sixteen hours. The suspension was filtered, in air, through Celite and the brown filtrate was reduced to dryness leaving a brown residue. Yield: 0.065 g (81 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 52.2 (d, $J_{PP}$ = 29 Hz), 41.5 (d, $J_{PP}$ = 29 Hz).

*(tt) [RuCl($PPh_3$)$_2$((S)-1-(pyridin-2-yl)ethanamine)]$BF_4$*



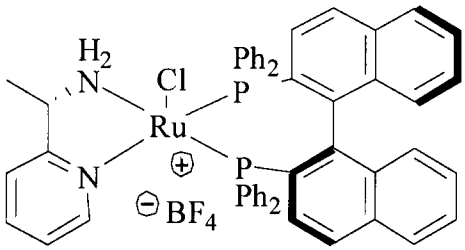

In an Ar filled flask, 0.100 g (0.12 mmol) of $RuCl_2(PPh_3)_2$((*S*)-1-(pyridin-2-yl)ethanamine) and 0.024 g (0.12 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (5 mL) was added and the resulting brown suspension was left to stir at ambient temperature for two hours. The suspension was filtered through a 0.45 μm PTFE syringe filter and the brown filtrate was reduced to dryness leaving a brown residue. Yield: 0.070 g (66 %). $^{19}F$ NMR (282 MHz, $CD_2Cl_2$): - 152 (s).

*(uu) [RuCl(S-XylylPPhos)((S)-1-(pyridin-2-yl)ethanamine)]$BF_4$*



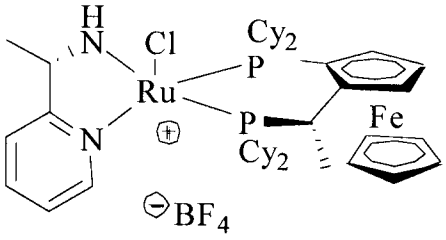
In an Ar filled flask, 0.150 g (0.14 mmol) of $RuCl_2$(*S*-XylylPPhos)((*S*)-1-(pyridin-2-yl)ethanamine) and 0.027 g (0.14 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (5 mL) was added and the resulting brown suspension was left to stir at ambient temperature for two hours. The suspension was filtered through a 0.45 μm PTFE syringe filter and the brown filtrate was reduced to dryness leaving a brown residue. Yield: 0.127 g (81 %). $^{19}F$ NMR (282 MHz, $CD_2Cl_2$): - 152 (s).

*(vv) [RuCl(R-BINAP)((S)-1-(pyridin-2-yl)ethanamine)]$BF_4$*



In an Ar filled flask, 0.150 g (0.16 mmol) of $RuCl_2$(*R*-BINAP)((*S*)-1-(pyridin-2-yl)ethanamine) and 0.032 g (0.16 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (5 mL) was added and the resulting brown suspension was left to stir at ambient temperature for two hours. The suspension was filtered through a 0.45 μm PTFE syringe filter and the brown filtrate was reduced to dryness leaving a brown residue. Yield: 0.087 g (55 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): No resolved peaks at ambient temperature. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$): - 152 (s).

*(ww) [RuCl($S_C$,$R_P$-$PCy_2$-$CH(CH_3)$-Fc-$PCy_2$)((S)-1-(pyridin-2-yl)ethanamine)]$BF_4$*



In an Ar filled flask, 0.075 g (0.08 mmol) of $RuCl_2$($S_C$,$R_P$-$PCy_2$-$CH(CH_3)$-Fc-$PCy_2$)((*S*)-1-(pyridin-2-yl)ethanamine) and 0.016 g (0.08 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (5 mL) was added and the resulting brown suspension was left to stir at ambient temperature for two hours. The suspension was filtered through a 0.45 μm PTFE syringe filter and the brown filtrate was reduced to dryness leaving a brown residue. Yield: 0.079 g (63 %). $^{19}F$ NMR (282 MHz, $CD_2Cl_2$): - 152 (s).

*(xx) [RuCl(R-binap)(R,R-cydn)]$CB_{12}H_{12}$*

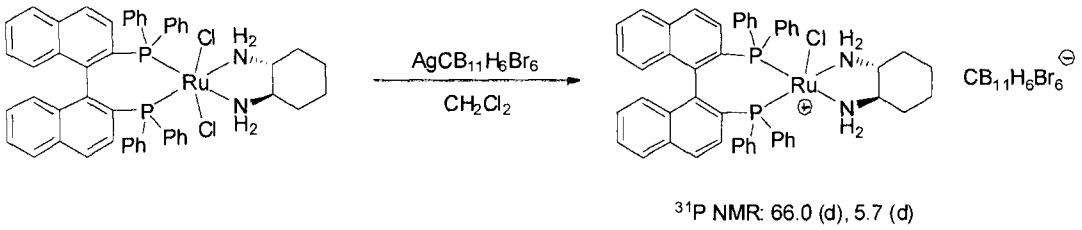
In the dry box, $RuCl_2$(Binap)(cydn) (0.18 g, 0.19 mmol) was dissolved in $CH_2Cl_2$ and $Ag(CB_{11}H_{12})$ (50 mg, 0.19 mmol) was dissolved in benzene and $CH_2Cl_2$. The two portions were then mixed and stirred for half hour. The AgCl then formed was filtered off and the compound was recrystallized from hexanes. Yield: 0.15 g, 74%.




$^{31}P$ NMR: 67.4 (d), 7.4 (d)

*(yy) [RuCl(R-binap)(R,R-cydn)]$CB_{12}H_6Br_6$*

In the dry box, $RuCl_2$(Binap)(cydn) (12.5 mg, 0.014 mmol) was dissolved in $CH_2Cl_2$ and $Ag(CB_{11}H_6Br_6)$ (10 mg, 0.014 mmol) was dissolved in benzene and $CH_2Cl_2$. The two portions were then mixed and stirred for half hour. The AgCl then formed was filtered off and the compound was recrystallized from hexanes. Yield: 15 mg, 73%.



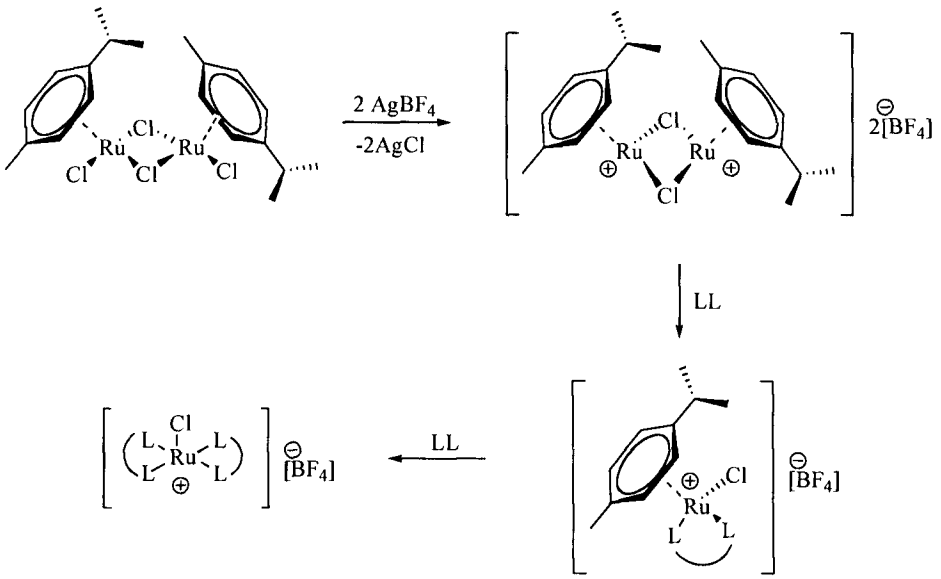

$^{31}$P NMR: 66.0 (d), 5.7 (d)

*Example 3: Alternate Route to Cationic Ruthenium Hydrogenation Catalysts*

In the syntheses described above, the neutral precursor complexes were treated with anion abstracting agents to render the complexes cationic. The neutral precursors were generally derived from the ubiquitous ruthenium compounds $[RuCl_2(p\text{-cymene})]_2$, $[RuCl_2(benzene)]_2$ or $[RuCl_2(cod)]_n$ (cod = cyclooctadiene). These are common synthons used to prepare a range of ruthenium complexes and are known to be notoriously insoluble materials. As a result of the insolubility of these complexes, the preparation of Ru derivatives from these material require long reaction times and forcing conditions.

An alternate route to the same cationic ruthenium hydrogenation catalysts exists in the use of a cationic Ru precursor. Indeed, a cationic derivative of $[RuCl_2(p\text{-cymene})]_2$ holds the promise of improved solubility and thus shorter reaction times and less forcing conditions. To this end, the reaction of $[RuCl_2(p\text{-cymene})]_2$ with anion abstracting agents was explored and found to yield the desired cationic synthon according to Scheme 2 below. The complexes $[Ru_2Cl_3(p\text{-cymene})_2][PF_6]$ and $[Ru(MeCN)_3(p\text{-cymene})]_2[BF_4]_2$ were described by Bennett et al., J. C. S. Dalton Trans. 1974, 233. Limited synthetic and spectroscopic details were provided in this report.

Scheme 2




*(a) [RuCl(p-cymene)]$_2$[BF$_4$]$_2$*

In an Ar filled flask, 0.25 g (0.041 mmol) [RuCl$_2$(*p*-cymene)]$_2$ and 0.16 g (0.082 mmol) of AgBF$_4$ were combined. $CH_2Cl_2$ (10 mL) was added and the resulting orange suspension was left to stir at ambient temperature. Within several minutes the suspension darkened to brown/green in colour. After 2 hours, the suspension was filtered through Celite and the orange filtrate was reduced to approximately 1 mL in volume. Addition of hexane afforded an oily orange solid which was washed repeatedly with hexane and dried in vacuo. Yield: 0.215 g (74 %).

*(b) In situ preparation of cationic ruthenium hydrogenation catalyst*

In an Ar filled flask, 0.070 g (0.11 mmol) [RuCl$_2$(*p*-cymene)]$_2$ and 0.045 g (0.11 mmol) of AgBF$_4$ were combined. $CH_2Cl_2$ (10 mL) was added and the resulting orange suspension was left to stir at ambient temperature. Within several minutes the suspension darkened to brown/green in colour. After 2 hours, the suspension was filtered through Celite and the orange filtrate was collected and set to stir. A solution of R-BINAP (0.142 g, 0.11 mmol) in toluene (5 mL) was added. The resulting solution was stirred for several minutes. Solid R,R-cydn (0.026 g, 0.11 mmol) was added. The resulting solution was heated to 60 °C for approximately 3

hours. The resulting solution was concentrated to dryness leaving an orange residue. A sample of the residue was employed in the catalytic hydrogenation of acetophenone according to the conditions described below. Result: time = 2 h; conv. = >99%; ee = 84%.

*Example 4: Second Alternate Route to Cationic Ruthenium Hydrogenation Catalysts*

Yet another route exists via an ill-defined mixture of ruthenium-diphosphine-DMF complexes (DMF = dimethylformamide) reported in the literature (Noyori et al., Tetrahedron Letters, 1991, 32, 4163). The mixture is believed to consist of the following components: $RuCl_2$(diphosphine)$(DMF)_2$ and $[RuCl_2$(diphosphine)$(DMF)]_n$). Thus, treatment of the $RuCl_2$(BINAP)$(DMF)_2$ and $[RuCl_2$(BINAP)$(DMF)]_n$) mixture with an equivalent of an anion abstracting agent (e.g. $AgBF_4$) to generate a cationic precursor which then react with a diamine (e.g. *R,R*-cydn) to yield the cationic ruthenium-diphosphine-diamine complex, [RuCl(*R*-BINAP)(*R,R*-cydn)]$BF_4$. This synthetic route is presented in Scheme 3 below. It should be noted that the product of this reaction also appears to be a mixture of the DMF-coordinated cation and the DMF-free cation.

Scheme 3

$$RuCl_2(BINAP)(DMF)_n \xrightarrow[2.\ R,R\text{-}cydn]{1.\ AgBF_4} [RuCl(BINAP)(R,R\text{-cydn})(DMF)_n]BF_4$$

n = 0, 1

This procedure can also be applied to the synthesis of compounds (I), (III) and (V) of this disclosure.

*(a) [$RuCl_2$(R-BINAP)$DMF)_n$]*

In an Ar filled flask, 0.250 g (0.50 mmol) of $[RuCl_2(C_6H_6)]_2$ and 0.622 g (1.00 mmol) of *R*-BINAP were combined. DMF (5 mL) was added and the resulting brown suspension was set to stir in a 100 °C oil bath. After 15 minutes, the suspension had cleared to a red/brown solution. The flask was removed from the oil bath and allowed to cool to RT. The solution was then concentrated to an oily residue and $Et_2O$ (20 mL) was added affording brick red solids. The solids were filtered off in

air, washed with $Et_2O$ (5 × 5 mL) and dried in vacuo. Yield: 0.820 g (87 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): several broad doublets between 50 - 62 ppm.

*(b) [RuCl(R-BINAP)(R,R-cydn)(DMF)$_n$]$BF_4$*

In an Ar filled flask, 0.200 g (0.21 mmol) of $RuCl_2$(*R*-BINAP)$(DMF)_2$ and 0.041 g (0.21 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (10 mL) was added and the resulting brown suspension was set to stir at ambient temperature. After 2 hours, 0.024 g (0.21 mmol) of *R,R*-cydn in $CH_2Cl_2$ (1 mL) was added and the suspension quickly changed to green in colour. The suspension was stirred for a further 2 hours and then filtered through a 0.45 mm PTFE syringe filter. The green filtrate was concentrated to approximately 1 mL and $Et_2O$ (20 mL) was added affording green solids. The solids were filtered off in air, washed with $Et_2O$ (4 × 5 mL) and dried in vacuo. Yield: 0.186 g (85 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 7.38 (d, $J_{PP}$ = 45 Hz), 67.4 (d, $J_{PP}$ = 45 Hz). These chemical shift values match those for the same compound prepared via treatment of $RuCl_2$(*R*-BINAP)(*R,R*-cydn) with one equivalent of $AgBF_4$. Minor peaks are also present between 48 – 54 ppm which are consistent with the presence of a small amount of a DMF adduct of the form "[RuCl(*R*-BINAP)(*R,R*-cydn)(DMF)]$BF_4$" which would account for the green colour (vs. orange for the same material prepared via treatment of $RuCl_2$(*R*-BINAP)(*R,R*-cydn) with $AgBF_4$).

*(c) [RuCl(R-BINAP)(R,R-cydn)(DMF)$_n$]$B(C_6F_5)_4$*

In an Ar filled flask, 0.200 g (0.21 mmol) of $RuCl_2$(*R*-BINAP)$(DMF)_2$ and 0.185 g (0.21 mmol) of $Li(OEt_2)_{2.5}[B(C_6F_5)_4]$ were combined. $CH_2Cl_2$ (10 mL) was added and the resulting brown suspension was set to stir at ambient temperature. After 2 hours, 0.024 g (0.21 mmol) of *R,R*-cydn in $CH_2Cl_2$ (1 mL) was added and the suspension gradually changed to green in colour. The suspension was stirred for a further 2 hours and then filtered through a 0.45 mm PTFE syringe filter. The green filtrate was concentrated to approximately 1 mL and hexane (20 mL) was added affording green solids. The solids were filtered off in air, washed with hexane (4 × 5 mL) and dried in vacuo. Yield: 0.333 g (96 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 7.31 (d, $J_{PP}$ = 45 Hz), 67.4 (d, $J_{PP}$ = 45 Hz). These chemical shift values match those for the same compound prepared via treatment of $RuCl_2$(*R*-binap)(*R,R*-cydn) with one equivalent of $Li(OEt_2)_{2.5}[B(C_6F_5)_4]$. Minor peaks are also present between 52 – 54 ppm which are consistent with a dmf adduct of the form "[RuCl(*R*-BINAP)(*R,R*-

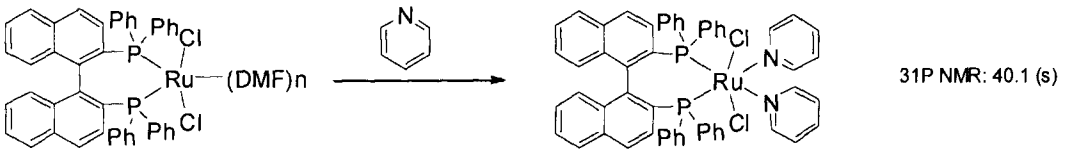
cydn)(DMF)]$B(C_6F_5)_4$" which would account for the green colour (vs. orange for the same material prepared via treatment of $RuCl_2$(*R*-BINAP)(*R,R*-cydn) with $Li(OEt_2)_{2.5}[B(C_6F_5)_4]$).

*Example 5: Third Alternate Route to Cationic Ruthenium Hydrogenation Catalysts*

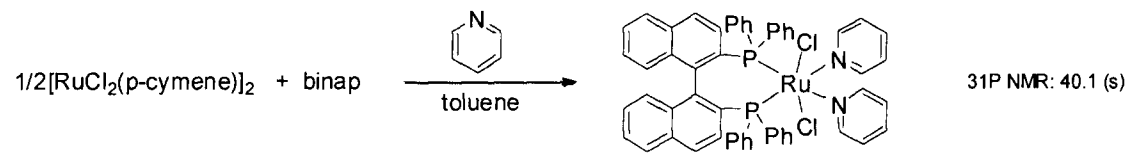
Another route to a cationic ruthenium catalyst exists through the stable precursor $RuCl_2$(diphosphine)$(pyridine)_2$. It has been determined that $RuCl_2$(diphosphine)$(pyridine)_2$ is a highly useful and convenient precursor to complexes of the type [RuCl(diphosphine)(diamine)LB]X and [RuCl(diphosphine)-(aminophosphine)LB]X. The precursor, $RuCl_2$(diphosphine)$(pyridine)_2$ is a well defined, single component (in contrast to the DMF analogue of Example 4). $RuCl_2$(diphosphine)$(pyridine)_2$ can be prepared from the corresponding DMF complex or in an analogous method to the preparation for the DMF complex wherein pyridine is used instead of DMF, as shown in Scheme 4.

Scheme 4

Route 1:

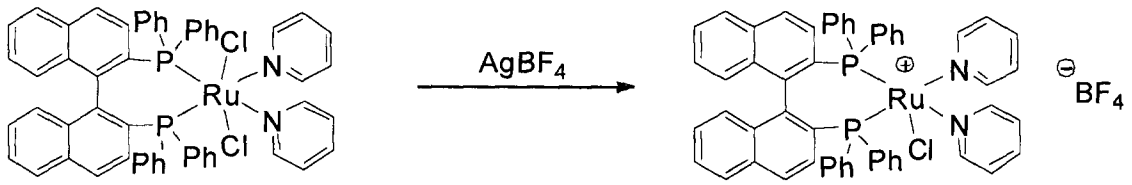



Route 2:




The precursor compound $RuCl_2$(diphosphine)$(pyridine)_2$ is readily derivatized into its cationic counterpart, [RuCl(diphopshine)$(pyridine)_2$]$BF_4$, by treatment with an anion abstracting agent (e.g. $AgBF_4$ as set out in Scheme 5).

Scheme 5

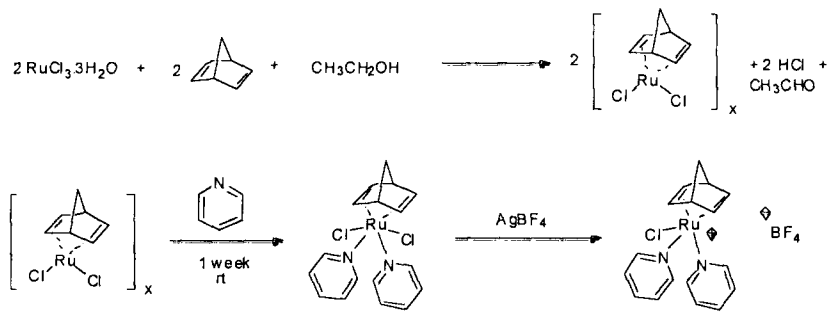



31P NMR: 53.2 (s)

The cation, an air stable solid which can be isolated in high yields and stored under ambient conditions, is a convenient precursor to other cationic hydrogenation catalysts. The cationic pyridine compound can be derivatized by treatment with a diamine into compounds of the type [RuCl(diphosphine)(diamine)]$BF_4$ (Examples 5(a) and (b)).

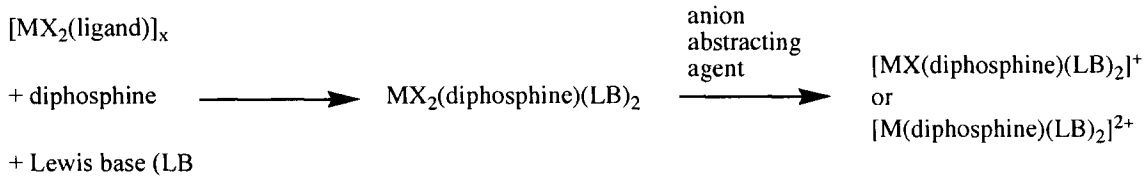
An alternate route to complexes of the type [RuCl(diphosphine)(pyridine)$_2$]$^+$ via a ruthenium-norbornadiene (NBD) complex which is equally valuable is outlined below in Scheme 6. It should be noted that pyridine can be replaced by any Lewis base and the product can be further derivatized to complexes of the type [RuCl(diphosphine)(diamine)LB]X and [RuCl(diphosphine)(aminophosphine)LB]X (where LB is Lewis base).

Scheme 6




The procedures described in this Example can be generalized into the following method for the preparation of cationic or dicationic catalysts:

Scheme 7

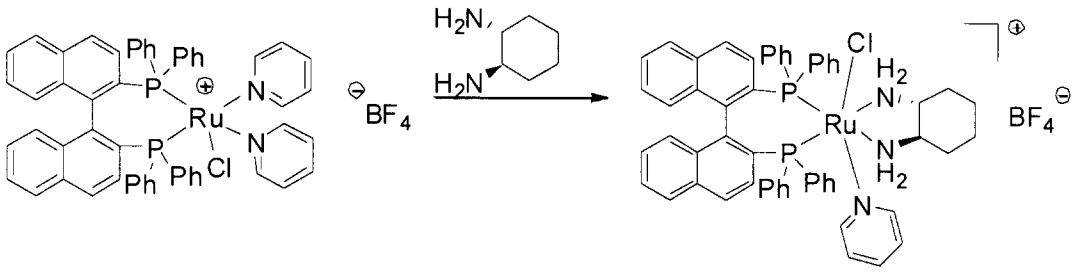



wherein M, X and LB are as defined for the compounds of the disclosure and diphosphine is a P2 ligand as defined for the compounds of the disclosure and ligand is a neutral displaceable ligand such as *p*-cymene, benzene, COD and NBD and x is an integer that depends on the structure of the complex (typically x is 2).

The cationic catalysts derived from the precursors described in this Example have been tested in hydrogenation using identical procedures as for the cations derived from treatment of the $RuCl_2$(diphosphine)(diamine) or $RuCl_2$(diphosphine)(PN) complexes with anion abstracting agents in the presence of Lewis bases. The complexes prepared via the $[RuCl(PP)(py)_2]BF_4$ precursor display essentially identical behavior in hydrogenation of acetophenone.

(a) $[RuCl(R\text{-binap})(R,R\text{-cydn})(py)]BF_4$

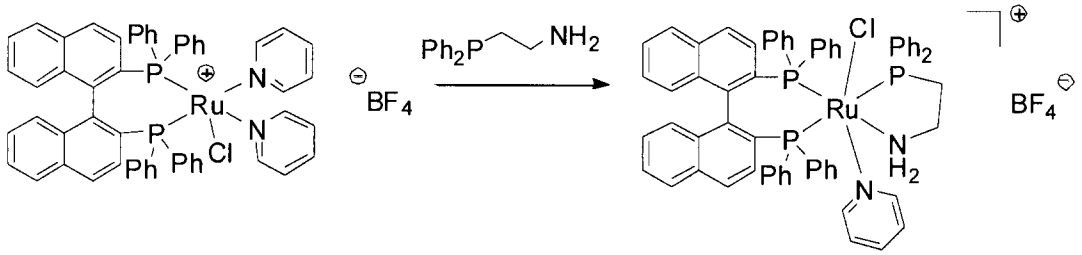
To a $CH_2Cl_2$ solution of $[RuCl(R\text{-binap})(py)_2]BF_4$ (0.08 g, 0.0796 mmol) was added a $CH_2Cl_2$ solution of the R-R-cydn (9.1 mg, 0.0796 mmol) under inert (Ar) atmosphere. The reaction mixture was allowed to stir overnight at ambient temperature. The solution was then concentrated, and the residue was recrystallized from $CH_2Cl_2/Et_2O$. The solid that precipitated was then filtered in air to obtain an amber-yellow color solid. Yield: 0.06 g, 70%. This catalyst was examined for its catalytic ability to convert acetophenone to its corresponding alcohol, and showed a 98% conversion with an enantiomeric excess of 80%.



31P NMR: 50.0 (d)
Hydrogenation: 98% conversion
(acetophenone) 80 % ee

*(b) [RuCl(R-binap)($Ph_2PCH_2CH_2NH_2$)(py)]$BF_4$*

To a $CH_2Cl_2$ solution of the [RuCl(R-binap)$(py)_2$]$BF_4$ (0.077 g, 0.0770 mmol) was added a $CH_2Cl_2$ solution of 2-(diphenylphosphino)ethylamine (17.6 mg, 0.0770 mmol) under inert atmosphere. The reaction mixture was allowed to stir overnight at ambient temperature. During this time some precipitate formed. The solution was then filtered, the filtrate was concentrated, and the residue was recrystallized from $CH_2Cl_2/Et_2O$. The solid that precipitated was then filtered in air to obtain an amber-yellow color solid. Yield: 0.05 g, 54%. This catalyst was examined for its catalytic ability to convert acetophenone to its corresponding alcohol, and showed a 72% conversion and an enantiomeric excess of 22%.



31P NMR: 53.4 (s)
Hydrogenation: 72% conversion
(acetophenone) 22 % ee

*(c) [RuCl(NBD)$(py)_2$]$BF_4$ (As per Scheme 6 above)*

The first step of the reaction is carried out in air. To a 500 mL schlenk flask containing a pear-shaped stirring bar is charged with a ethanol solution (200 mL) of $RuCl_3.3H_2O$, and bicycle [2.2.1] hepta-2,5-diene (norbornadiene) (10 mL,

0.12 mol). The mixture is vigorously stirred at room temperature for 24 hour. During this time the brick red to brown solid precipitated from the solution. On completion of the reaction the suspension is filtered using a medium porosity glass filter frit and washed thoroughly with acetone (50 mL). Drying of the solid gives 3.8 g of insoluble brick red solid. *(ref: Inorganic Syntheses. New York: John Wiley and Sons, 1989: 250 – 251)*

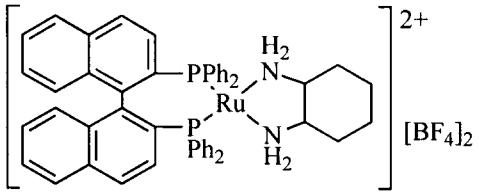
The second step of the reaction is carried out under Argon and the work-up procedure was slightly modified from the original literature. $[(NBD)RuCl_2]_x$ (2.0 g, 7.57 mmol) was rapidly stirred in pyridine (50 mL) for 1 week at room temperature under argon. The mixture changed from brown to greenish-yellow over this period. The pyridine was then removed under vacuum to give a greenish yellow solid. The solid was then dissolved in $CH_2Cl_2$ and the insoluble black material was filtered off. The $CH_2Cl_2$ solution was then concentrated, and recrystallized from hexanes 2 times, yielding a dark-orange crystalline materials. Yield: 3.0 (93%). $^1H$ NMR (400 MHz, $CD_2Cl_2$): d 1.55 (br s, 2H, $CH_2$), 4.05 ( br s, 2H, bridgehead CH), 4.85 (m, 4H, olefin), 7.25 (br t, J = 11.9 Hz, 4H), 7.7 (br t, J = 11.9 Hz, 2H), 8.54 ( br d, J = 12.0 Hz, 4H).*(ref: Chirality 2000, 12: 514 – 522)*

The third step of the reaction is carried out in the dry box. To a small vial is charged $(NBD)RuCl_2(Pyridine)2$ (0.1 g, 0.23 mmol) and 1 equiv. of $AgBF_4$ (46 mg, 0.23 mmol) and $CH_2Cl_2$ (5 mL). The solution was allowed to stir for 1 hour. Precipitate was observed during this period. The precipitate was then filtered off, and the filtrate was concentrated and recrystallized from $Et_2O$ to obtain a pale greenish-yellow solid. Yield: 80 mg, 72%.

*Example 6: Synthesis of Dicationic Ruthenium Hydrogenation Catalysts*

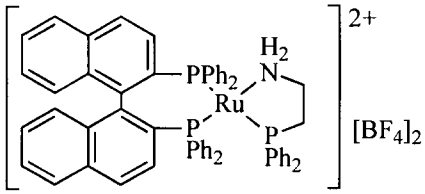
*(a) $[Ru(R\text{-}binap)(R,R\text{-}cydn)][BF_4]_2$*

In an Ar filled flask, 0.100 g (0.11 mmol) of $RuCl_2$(R-binap)(R,R-cydn) and 0.045 g (0.24 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (7 mL) was added and the resulting rust coloured suspension was left to stir at ambient temperature for two hours after which time it was filtered through Celite. The orange filtrate was reduced to dryness leaving a yellow/orange residue. Yield: 0.085 g (77 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 0.48 (d, $J_{PP}$ = 39 Hz), 64.89 (d, $J_{PP}$ = 39 Hz).



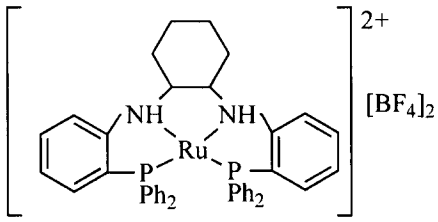
*(b) [Ru (R-binap)($Ph_2PCH_2CH_2NH_2$)][$BF_4$]$_2$*

In an Ar filled flask, 0.115 g (0.11 mmol) of $RuCl_2$(R-binap)($Ph_2PCH_2CH_2NH_2$) and 0.044 g (0.24 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (7 mL) was added and the resulting dark orange suspension was left to stir at ambient temperature for two hours after which time it was filtered through Celite. The yellow filtrate was concentrated to approximately 1 mL in volume and $Et_2O$ was added (10 mL) affording pale yellow solids. The solids were filtered off, washed with $Et_2O$ (3 x 5 mL) and dried in vacuo. Yield: 0.119 g (94 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): 15.3 (d, $J_{PP}$ = 18 Hz), 17.2 (d, $J_{PP}$ = 18 Hz), 62.2 (br m).



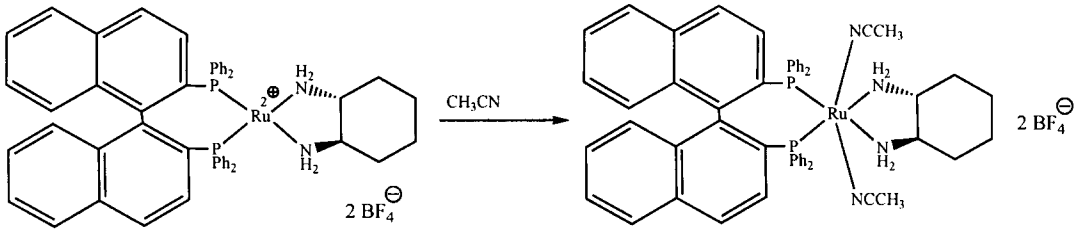
*(c) [Ru(R,R-DPPcydn)][$BF_4$]$_2$*

In an Ar filled flask, 0.200 g (0.20 mmol) of $RuCl_2$(R,R-DPPcydn) and 0.093 g (0.48 mmol) of $AgBF_4$ were combined. $CH_2Cl_2$ (7 mL) was added and the resulting dark yellow/green suspension was left to stir at ambient temperature for two hours after which time it was filtered through Celite. The yellow filtrate was concentrated to approximately 1 mL in volume and $Et_2O$ was added (10 mL) affording pale yellow solids. The solids were filtered off, washed with $Et_2O$ (3 x 5 mL) and dried in vacuo. Yield: 0.169 g (92 %). $^{31}P$ NMR (ppm, $CD_2Cl_2$): broad signals at 42.2 and 63.3 ppm barely discernable above baseline.



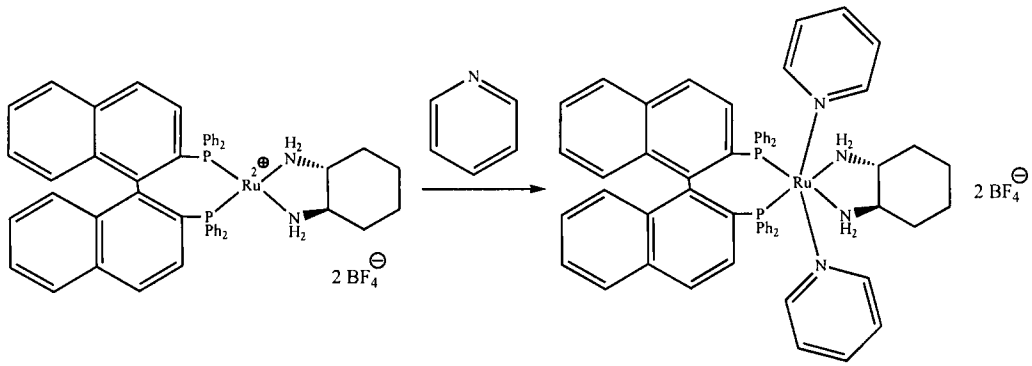
*Example 7: Lewis Base Adducts of Dicationic Catalysts*

*(a)*



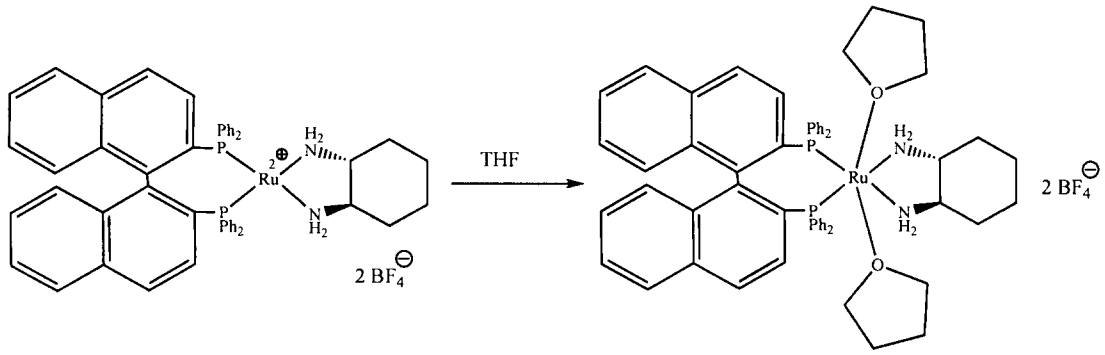
$^{31}P$ NMR: 49.8 (d), 42.9 (s), 42.1 (d).

*(b)*



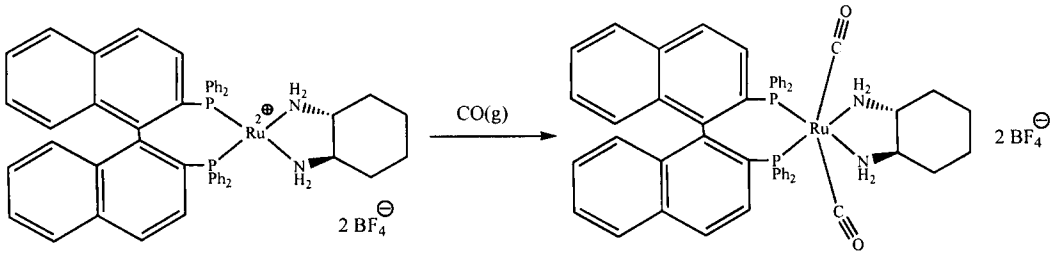
$^{31}P$ NMR: 61.4 (d), 59.2 (d), 51.9 (s), 46.6 (d), 44.8 (d).

*(c)*



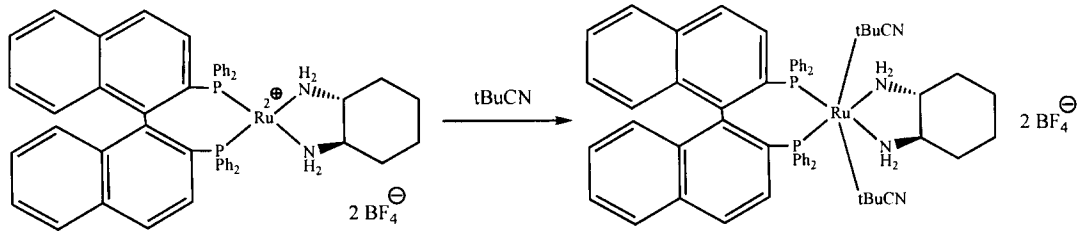
$^{31}P$ NMR: 62.2 (br), 42.2 (br).

*(d)*



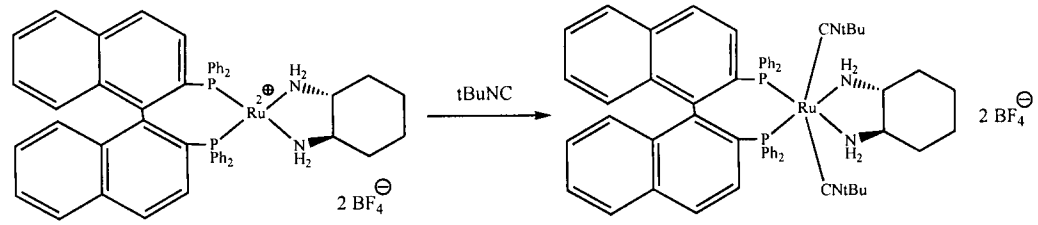

$^{31}$P NMR: 31.3 (s), 31.1 (s), 29.8 (d), 24.6 (d).

*(e)*




$^{31}$P NMR: 50.4 (d), 42.3 (s), 41.4 (d).

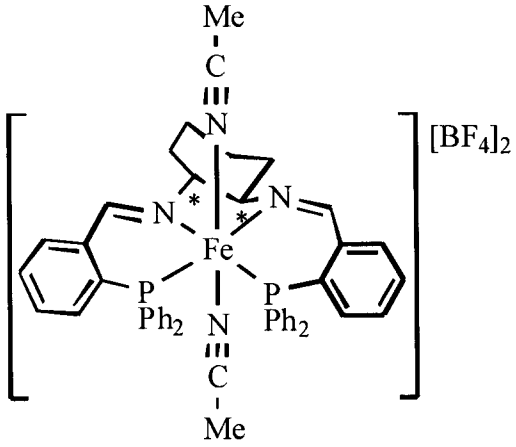
*(f)*




$^{31}$P NMR: 42.4 (d), 42.4 (s), 33.0 (d).

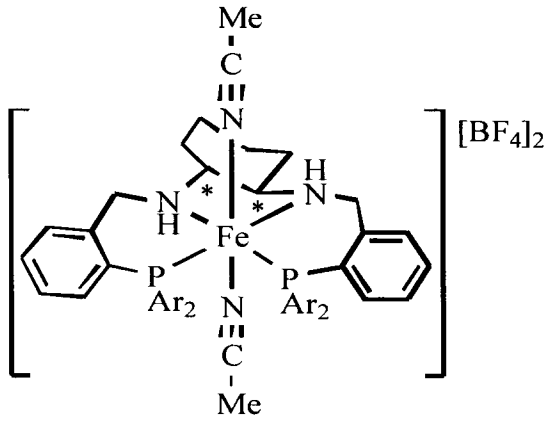
*Example 8: Cationic Iron Hydrogenation Catalysts*

*(a) Bis(acetonitrile) $N^1$,$N^2$-bis(2-(diphenylphosphino)benzylidene)(R,R)-cyclohexane-1,2-diamine iron(II)tetrafluoroborate, $[Fe(NCMe)_2((R,R)\text{-}cyPPh_2N_2)][BF_4]_2$,*




Acetonitrile (5 mL) was added to 210 mg (0.319 mmol) of $N^1$,$N^2$-bis(2-(diphenylphosphino)benzylidene)cyclohexane-1,2-diamine, (*R*,*R*)-$cyP_2N_2$ and 102 mg (0.302 mmol) of iron (II) tetrafluoroborate hexahydrate $[Fe(OH_2)_6][BF_4]_2$ and the mixture was stirred for one hour. The solution was concentrated to ca. 1 mL and then 20 mL of diethyl ether was added dropwise. The mixture was stirred for 30 minutes and then the solid was collected on a glass frit and dried in vacuo. Yield: 240 mg, 82 %. $^{31}P\{^1H\}$ NMR (121 MHz, $CD_3CN$): 52.7 ppm.

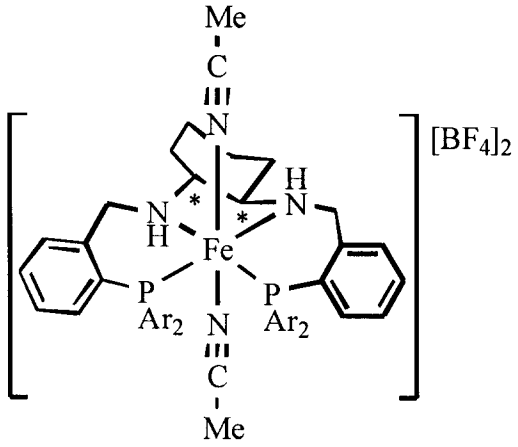
*(b) Bis(acetonitrile) $N^1,N^2$-bis(2-(ditolylphosphino)benzyl)(R,R)-cyclohexane-1,2-diamine iron(II)tetrafluoroborate, $[Fe(NCMe)_2((R,R)\text{-}cyPAr_2(NH)_2)][BF_4]_2$*




Ar = 4-$MeC_6H_4$

A solution of $N^1,N^2$-bis(2-(ditolylphosphino)benzyl)(*R,R*)-cyclohexane-1,2-diamine (*R,R*)-$cyPAr_2(NH)_2$ (149 mg, 0.207 mmol) and iron (II) tetrafluoroborate hexahydrate $[Fe(OH_2)_6][BF_4]_2$ (70 mg, 0.207 mmol) was stirred at r.t. in MeCN (5 mL) for 20 min. The resulting purple solution was concentrated to 1 mL and 10 mL of $Et_2O$ were added. A purple powder precipitated and was isolated by filtration. Yield: 170 mg, 87%. $^{31}P\{^1H\}$ NMR (121 MHz, $CD_3CN$): 35.3 ppm.

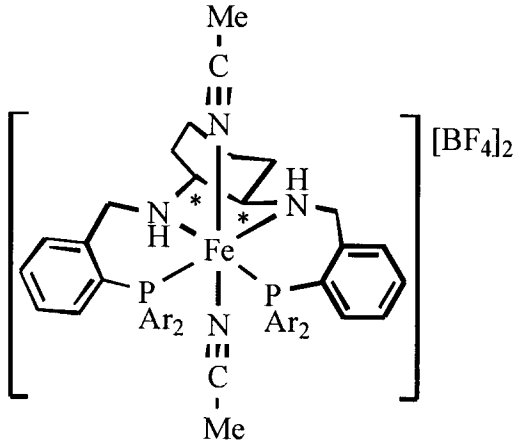
*(c) Bis(acetonitrile) $N^1,N^2$-bis(2-(dixylylphosphino)benzyl)(R,R)-cyclohexane-1,2-diamine iron(II)tetrafluoroborate, $[Fe(NCMe)_2((R,R)\text{-}cyPAr_2(NH)_2)][BF_4]_2$*




Ar = 3,5-$Me_2C_6H_3$

A solution of $N^1,N^2$-bis(2-(dixylylphosphino)benzyl)(*R,R*)-cyclohexane-1,2-diamine (*R,R*)-cyP$Ar_2(NH)_2$ (161 mg, 0.207 mmol) and iron (II) tetrafluoroborate hexahydrate $[Fe(OH_2)_6][BF_4]_2$ (70 mg, 0.207 mmol) was stirred at r.t. in MeCN (5 mL) for 20 min. The resulting purple solution was concentrated to 1 mL and 10 mL of $Et_2O$ were added. A purple powder precipitated and was isolated by filtration. 3: Yield: 190 mg, 91%. $^{31}P\{^1H\}$ NMR (121 MHz, $CD_3CN$): 39.2 ppm.

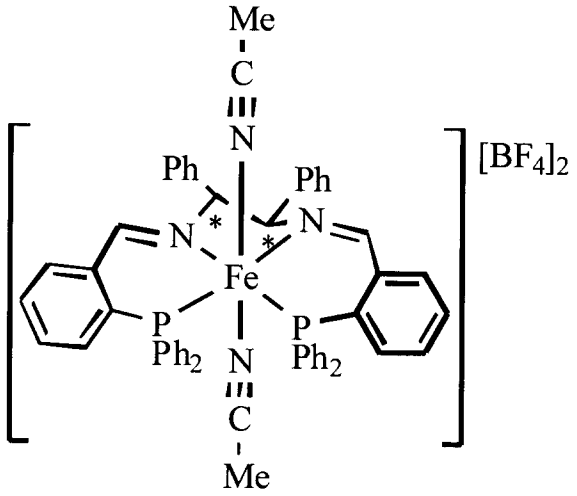
*(d) Bis(acetonitrile) $N^1,N^2$-bis(2-(3,5-di-tert-butyl-4-methoxy-phenylphosphino)benzyl)(R,R)-cyclohexane-1,2-diamine iron(II)tetrafluoroborate, $[Fe(NCMe)_2((R,R)\text{-}cyPAr_2(NH)_2)][BF_4]_2$*




Ar = 3,5-$Me_2$-4-OMe-$C_6H_2$

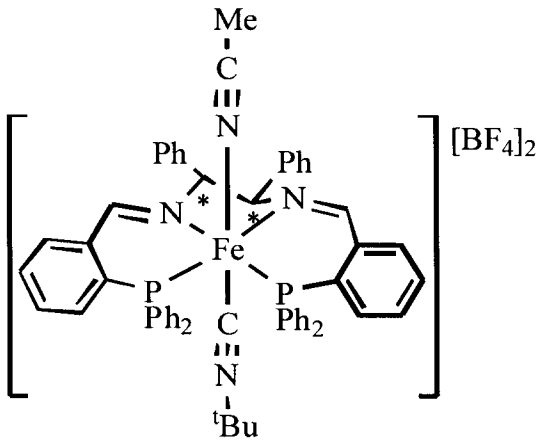
A solution of $N^1,N^2$-bis(2-(3,5-di-tert-butyl-4-methoxy-phenylphosphino)benzyl)(*R,R*)-cyclohexane-1,2-diamine (*R,R*)-cyP$Ar_2(NH)_2$ (255 mg, 0.207 mmol) and iron (II) tetrafluoroborate hexahydrate $[Fe(OH_2)_6][BF_4]_2$ (70 mg, 0.207 mmol) was stirred at r.t. in MeCN (5 mL) for 20 min. The resulting brown solution was concentrated to 1 mL and 10 mL of $Et_2O$ were added. A beige-brown powder precipitated and was isolated by filtration. Yield: 190 mg, 91%. $^{31}P\{^1H\}$ NMR (121 MHz, $CD_3CN$): 47.5 ppm.

*(e) Bis(acetonitrile) $N^1,N^2$-bis(2-(diphenylphosphino)benzylidene)(R,R)-diphenylethylene-1,2-diamine iron(II)tetrafluoroborate, $[Fe(NCMe)_2((R,R)\text{-}dpenPPh_2N_2)][BF_4]_2$*



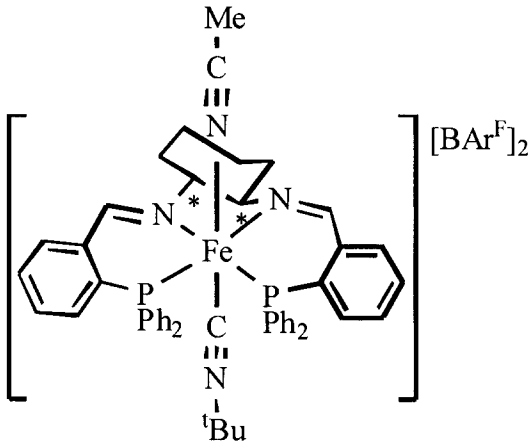

Synthesis of $[Fe(NCMe)_2((R,R)\text{-}dpenPPh_2N_2)][BF_4]_2$, (5). A solution of (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine (63 mg, 0.297 mmol), 2-(diphenylphosphino)benzaldehyde (172 mg, 0.593 mmol), and iron (II) tetrafluoroborate hexahydrate $[Fe(OH_2)_6][BF_4]_2$ (100 mg, 0.296 mmol) was stirred overnight under reflux in MeCN (5 mL). The red orange solution was concentrated to 1 mL and 10 mL of $Et_2O$ were added. A red-orange powder precipitated and was isolated by filtration. Yield: 290 mg, 92%. $^{31}P\{^1H\}$ NMR (121 MHz, $CD_3CN$): 52.3 ppm.

*(f) [Fe(CN$^t$Bu)(NCMe)((R,R)-dpenPPh$_2$N$_2$)][BF$_4$]$_2$*




A solution of [Fe(NCMe)$_2$((*R,R*)-dpen-PPh$_2$N$_2$)][BF$_4$]$_2$ (130 mg, 0.122 mmol) and *t*BuNC (14 μL, 0.122 mmol) in acetone (3 mL) was stirred for 15 min. The resulting orange-yellow solution was evaporated to dryness to give an orange powder). 6: Yield: 55 mg, 41%. $^{31}$P{$^1$H} NMR (121 MHz, $CD_3CN$): 56.1 ($^2J_{P\text{-}P}$ = 48 Hz), 44.8 ($^2J_{P\text{-}P}$ = 48 Hz) ppm.

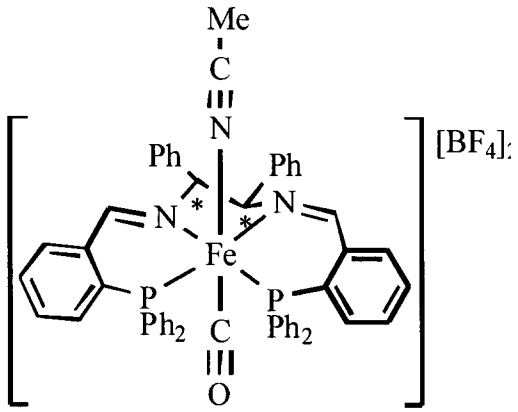
*(g) [Fe(CN$^t$Bu)(NCMe)((R,R)-cyPPh$_2$N$_2$)][BAr$^F$]$_2$*




A solution of [Fe(NCMe)$_2$((*R,R*)-cy-PPh$_2$N$_2$)][BF$_4$]$_2$ (40 mg, 0.039 mmol) and NaBAr$^F$ (71 mg, 0.079 mmol) in dichloromethane (5 mL) was stirred for 1 hour. The resulting orange-yellow solution was filtered on celite and evaporated to

dryness to give an orange powder. 7: Yield: 90 mg, 89%. $^{31}P\{^{1}H\}$ NMR (121 MHz, $CD_3CN$): 55.2 ($^{2}J_{P-P}$ = 54 Hz), 48.1 ($^{2}J_{P-P}$ = 54 Hz) ppm.

*(h) [Fe(CO)(NCMe)((R,R)-dpenPPh$_2$N$_2$)][BF$_4$]$_2$,*



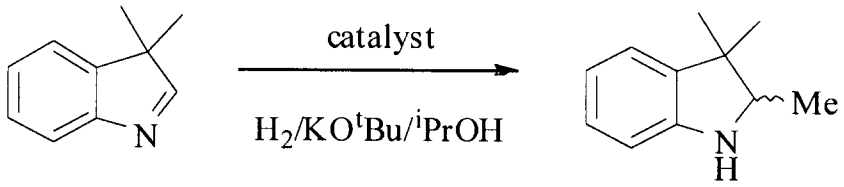

A solution of Fe(NCMe)$_2$((*R,R*)-dpenPPPh$_2$N$_2$)][BF$_4$]$_2$ (185 mg, 0.173 mmol) in acetone (10 mL) was stirred under CO overnight. The resulting orange solution was evaporated to dryness to give an orange powder. The NMR of the crude product shows an AB pattern characteristic of the formation of [Fe(CO)(NCMe)((*R,R*)-dpenPh$_2$N$_2$)][BF$_4$]$_2$, (7) (purity < 50%) with other unidentified impurities. $^{31}P\{^{1}H\}$ NMR (121 MHz, $CD_3CN$): 52.9 ($^{2}J_{P-P}$ = 40 Hz), 49.7 ($^{2}J_{P-P}$ = 40 Hz), 9.1, -2.4, -19.6, -22.1 ppm.

*Example 9: General Procedure for Hydrogenation with Ruthenium Complexes*

A solution of acetophenone (1.0 g, 8.3mmol) in 2-propanol (10ml) was added to a 50 mL Schlenk flask. After evacuating and refilling with argon, a mixture of catalyst (e.g. [RuCl(R-binap)(R,R-cydn)]BF$_4$; 0.01mmol) and K$^{t}$OBu (20 mg, 0.18mmol) was added. The resulting mixture was then injected into a 100 mL autoclave which had been previously placed under an atmosphere of $H_2$. The autoclave was pressurized to 200 psig and the reaction mixture was stirred at ambient temperature. The reaction progress was monitored by TLC. Upon completion of the reaction, the solvent was removed under vacuum and the mixture was filtered through silica gel (ca. 6 cm) using 3:1 hexane:ethyl acetate. The solvent was removed from

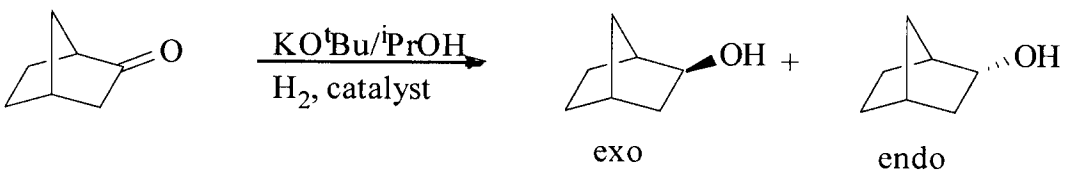
the filtrate affording the product as a colorless liquid. Results are shown in Tables 1-9.

*Example 10: Hydrogenation of 2,3,3-trimethylindolenine*




A solution of 2,3,3-trimethylindolenine (0.286 g, 1.8 mmol) in 2-propanol (10 mL) was added to a 50 mL Schlenk flask. After evacuating and refilling with argon, a mixture of catalyst (0.01 mmol) and $KO^tBu$ (29 mg, 0.26 mmol) was added. The resulting mixture was then injected into a 100 mL autoclave which had been previously placed under an atmosphere of $H_2$. The autoclave was pressurized to 150 psi and the reaction mixture was stirred at ambient temperature. A solution of $Na_2CO_3$ was added to render the mixture basic. The product was extracted with $CH_2Cl_2$. The resulting organic phases were dried on $MgSO_4$, filtered and evaporated to dryness. The $^1H$ NMR analysis was used to calculate the conversion. The sample was purified by chromatography on silica gel using hexane and ethyl acetate and submitted for HPLC analysis to determine the e.e. The results are presented in Table 10.

*Example 11: Hydrogenation of Norcamphor*




A solution of norcamphor (0.64 g, 5.82 mmol) in 2-propanol (5 mL) was added to a 50 mL Schlenk flask. After evacuating and refilling with argon, a

mixture of catalyst (i.e. $[RuCl(Ph_2PCH_2CH_2NH_2)_2]BF_4$; 0.010 g, 0.015 mmol) and K$^t$OBu (0.02 g, 0.18 mmol) in 2-propanol (5 mL) was added. The resulting mixture was then injected into a 100 mL autoclave which had been previously placed under an atmosphere of $H_2$. The autoclave was pressurized to 200 psig and the reaction mixture was stirred at ambient temperature. The reaction progress was monitored $^1$H NMR. Results for $[RuCl(Ph_2PCH_2CH_2NH_2)_2]BF_4$: 99:1 endo:exo.

*Example 12: Hydrogenation of acetophenone using cationic iron complexes*

*(a) $H_2$ conditions*

Under argon, a solution of degassed acetophenone (120 mg, 1 mmol) and KO$^t$Bu (4.5 mg, 0.04 mmol) was added to a Schlenk flask. The resulting mixture was then injected into a 100 mL autoclave which already contains the iron catalyst (5 mg, 0.005 mmol) and 6 mL of degassed 2-propanol. under an atmosphere of $H_2$. The autoclave was pressurized to 25 atm and the reaction mixture was stirred at 50 °C. After 17 hours, the sample was then filtered through silica gel (ca. 2 cm) using $CH_2Cl_2$ and submitted for GC analysis. The results are shown in Table 11.

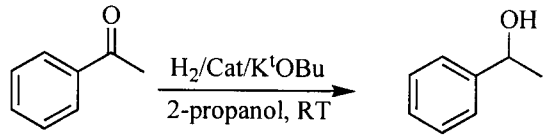
*(b) Transfer hydrogenation conditions*

Under argon, the iron complex (5 mg, 0.005 mmol), KO*t*Bu (5 mg, 0.045 mmol) and acetophenone (120 mg, 200 equiv) were stirred in 5 mL of 2-propanol at r.t. The sample was then filtered through silica gel (ca. 2 cm) using $CH_2Cl_2$ and submitted for GC analysis. The results are shown in Table 12.

While the present disclosure has been described with reference to what are presently considered to be the preferred examples, it is to be understood that the disclosure is not limited to the disclosed examples. To the contrary, the disclosure is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

All publications, patents and patent applications are herein incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety. Where a term in the present application is found to be defined differently in a document incorporated herein by reference, the definition provided herein is to serve as the definition for the term.

TABLE 1. RESULTS OF THE HYDROGENATION OF ACETOPHENONE CATALYSED BY CATIONIC COMPLEXES OF RUTHENIUM




5

| Entry | Complex | Time(h) | Conv.(%) | ee (%) |
|---|---|---|---|---|
| 1 | [RuCl(*R*-binap)(*R,R*-cydn)]$BF_4$ | 1 | >99 | 80 |
| 2 | [RuCl(*R*-binap)(*R,R*-cydn)$CH_3CN$]$BF_4$ | 17 | >99 | 84 |
| 3 | [RuCl(*R*-binap)(*R,R*-cydn)py] $BF_4$ | 17 | >99 | 83 |
| 4 | [RuCl(*R*-binap)(*R,R*-cydn)][$B(C_6F_5)_4$] | 17 | >99 | 82 |
| 5 | [RuCl(*R*-binap)($Ph_2PCH_2CH_2NH_2$)]$BF_4$ | 2 | >99 | 84 |
| 6 | [RuCl(*R*-binap)($Ph_2PCH_2CH_2NH_2$)]$B(C_6F_5)_4$ | 2 | >99 | 83 |
| 7 | [RuCl(S-binap)(S,S-$Ph_2PCH(Ph)CH(Ph)NH_2$)]$BF_4$ | 17 | >99 | 26 |
| 8 | [RuCl(*R*-binap)(S,S-$Ph_2PCH(Ph)CH(Ph)NH_2$)]$BF_4$ | 3 | >99 | 69 |
| 9 | [RuCl($Ph_2PCH_2CH_2NH_2)_2$]$BF_4$ | 1 | >99 | n/a |
| 10 | [RuCl($Ph_2PCH_2CH_2NH_2)_2$][$B(C_6F_5)_4$] | 0.5 | >99 | n/a |
| 11 | [RuCl(*R*-tolbinap)(R,R - $Ph_2PCH(Ph)CH(CH_3)NH_2$]$BF_4$ | 7 | 70 | 52 |
| 12 | [RuCl(*R*-tolBinap)(R,R - $Ph_2PCH(Ph)CH(CH_3)NH_2$][$B(C_6F_5)_4$] | 8 | >99 | 51 |
| 13 | [RuCl(*R*-3,5-xylylbinap)(R,R - $Ph_2PCH(Ph)CH(CH_3)NH_2$]$BF_4$ | 17 | 70 | 20 |
| 14 | [RuCl(*R*-3,5-xylylbinap)(R,R - $Ph_2PCH(Ph)CH(CH_3)NH_2$][$B(C_6F_5)_4$] | 7 | 60 | 33 |
| 15 | [RuCl($PPh_3)_2$(NH2CH2-Py)]$BF_4$ | 3 | >99 | n/a |
| 16 | [RuCl($PPh_3)_2$($NH_2CH_2$-Py)][$B(C_6F_5)_4$] | 3 | >99 | n/a |
| 17 | [RuCl(*R*-Binap)(Sc,Rp-$NH_2$-$CH(CH_3)$-Fc-$PPh_2$)]$BF_4$ | 22 | 41 | 15 |
| 18 | [RuCl(*R*-Binap)(Rc,Sp-$NH_2$-$CH(CH_3)$-Fc-$PPh_2$)]$BF_4$ | 22 | 85 | 0.5 |

| | | | | |
|---|---|---|---|---|
| 19 | [RuCl(*R*-Binap)(Sc,Rp-$NH_2$-$CH(CH_3)$-Fc-$PPh_2$)]$B(C_6F_5)_4$ | 22 | 38 | 6.4 |
| 20 | [RuCl(*R*-Binap)(Rc,Sp-$NH_2$-$CH(CH_3)$-Fc-$PPh_2$)][$B(C_6F_5)_4$] | 22 | 63 | 14 |
| 21 | [RuCl(1R,2*R*-$(Ph_2PC_6H_4CH_2NH)_2C_6H_{10}$)]$BF_4$ | 1.5 | >99 | 24.3 |
| 22 | [RuCl(1R,2*R*-$(Ph_2PC_6H_4CH_2NH)_2C_6H_{10}$)] [$B(C_6F_5)_4$] | 1.5 | >99 | 6.7 |
| 23 | [RuCl(1R,2*R*-(4-methyl-$Ph_2PC_6H_4CH_2NH)_2C_6H_{10}$)]$BF_4$ | 1.5 | >99 | 23.5 |
| 24 | [RuCl(1R,2*R*-(4-methyl-$Ph_2PC_6H_4CH_2NH)_2C_6H_{10}$)][$B(C_6F_5)_4$] | 1.5 | >99 | 6.4 |
| 25 | [RuCl(1R,2*R*-(3,5-dimethyl-$Ph_2PC_6H_4CH_2NH)_2C_6H_{10}$)]$BF_4$ | 1.5 | >99 | 73 |
| 26 | [RuCl(1R,2*R*-(3,5-dimethyl-$Ph_2PC_6H_4CH_2NH)_2C_6H_{10}$)][$B(C_6F_5)_4$] | 1.5 | >99 | 74.5 |
| 27 | $RuCl_2$(S-PPhos)(S-DAIPEN) (Comparative Example) | 5 | >99 | 71 |
| 28 | [RuCl(S-PPhos)(S-DAIPEN)]$BF_4$ | 4 | >99 | 89.3 |
| 29 | [RuCl(S-PPhos)(S-DAIPEN)]$B(C_6F_5)_4$ | 4 | >99 | 88.7 |
| 30 | $RuCl_2$(S-xylylPPhos)(S-DAIPEN) (Comparative Example) | 3 | >99 | 97.3 |
| 31 | [RuCl(S-xylylPPhos)(S-DAIPEN)]$BF_4$ | 4 | >99 | 99.3 |
| 32 | [RuCl(S-xylylPPhos)(S-DAIPEN)]$B(C_6F_5)_4$ | 4 | >99 | 98.7 |
| 33 | $RuCl_2$(S-BINAP)(S-DAIPEN) (Comparative Example) | 3 | >99 | 87 |
| 34 | [RuCl(S-BINAP)(S-DAIPEN)]$BF_4$ | 4 | >99 | 85 |
| 35 | [RuCl(S-BINAP)(S-DAIPEN)]$B(C_6F_5)_4$ | 4 | >99 | 87 |
| 36 | [$RuCl_2$(S-PhanePhos)(R,R-DPEN)] (Comparative Example) | 3 | >99 | 95.6 |
| 37 | [RuCl(S-PhanePhos)(R,R-DPEN)]$BF_4$ | 3 | >99 | 97.5 |
| 38 | [RuCl(S-PhanePhos)(R,R-DPEN)]$B(C_6F_5)_4$ | 3 | >99 | 98 |
| 39 | [$RuCl_2$(S-XylylPhanePhos)(R,R-DPEN)] (Comparative Example) | 3 | >99 | 96.8 |
| 40 | [RuCl(S-XylylPhanePhos)(R,R-DPEN)]$BF_4$ | 3 | >99 | 96.6 |
| 41 | [RuCl(S-XylylPhanePhos)(R,R-DPEN)]$B(C_6F_5)_4$ | 3 | >99 | 97.8 |
| 42* | [$RuCl(PPh_3)_2$((S)-1-(pyridin-2- | 1.5 | 65 | 15.5 |

| | | | | |
|---|---|---|---|---|
| | yl)ethanamine)]$BF_4$ | 5 | >99 | 15.5 |
| 43* | [RuCl(S-XylylPPhos)((S)-1-(pyridin-2-yl)ethanamine)]$BF_4$ | 3 | >99 | 53 |
| 44* | [RuCl(R-BINAP)((S)-1-(pyridin-2-yl)ethanamine)]$BF_4$ | 3 | >99 | 3 |
| 45* | [RuCl($S_C$,$R_P$-$PCy_2$-$CH(CH_3)$-Fc-$PCy_2$)((S)-1-(pyridin-2-yl)ethanamine)]$BF_4$ | 1.5 | >99 | 23.7 |
| 46 | [RuCl(*R*-binap)(*R,R*-cydn)$(dmf)_n$]$BF_4$ | 4 | 100 | 82 |
| 47 | [RuCl(*R*-binap)(*R,R*-cydn)$(dmf)_n$]$B(C_6F_5)_4$ | 4 | 100 | 80 |

Substrate:Ru = 830, $P_{H2}$=160Psi. *Substrate:Ru:Base = 1000:1:12, $P_{H2}$ = 170 psi

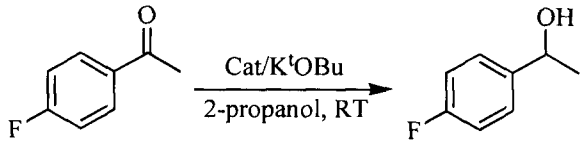
5

TABLE 2. RESULTS OF THE HYDROGENATION OF ACETOPHENONE CATALYSED BY CATIONIC COMPLEXES OF RUTHENIUM COMPARING DIFFERENT COUNTER ANIONS.

| Entry | Cat | Time (h) | Conv. (%) | ee (%) |
|---|---|---|---|---|
| 1 | (*R*-binap)$RuCl_2$(*R*,*R*-dach) | 17 | >99 | 83 |
| 2 | [(*R*-binap)RuCl(*R*,*R*-dach)]$BF_4$ | 1 | >99 | 80 |
| 3 | [(*R*-binap)RuCl(*R*,*R*-dach)]$PF_6$ | 17 | >99 | 78 |
| 4 | [(*R*-binap)RuCl(*R*,*R*-dach)]OTf | 17 | >99 | 78 |
| 5 | [(*R*-binap)RuCl(*R*,*R*-dach)]$B(C_6F_5)_4$ | 17 | >99 | 82 |
| 6 | [(*R*-binap)RuCl(*R*,*R*-dach)][$B(3,5\text{-}(CF_3)_2C_6H_3)_4$] | 17 | >99 | 82 |
| 7 | (*R*-binap)$RuCl_2$(PGly) | 17 | >99 | 23 |
| 8 | [(*R*-binap)RuCl(PGly)]$BF_4$ | 2 | >99 | 84 |
| 9 | [(*R*-binap)RuCl(PGly)]$PF_6$ | 17 | 99 | 73 |
| 10 | [(*R*-binap)RuCl(PGly)]OTf | 17 | >99 | 30 |
| 11 | [(*R*-binap)RuCl(PGly)]$B(C_6F_5)_4$ | 2 | >99 | 83 |
| 12 | [(*R*-binap)RuCl(PGly)][$B(3,5\text{-}(CF_3)_2C_6H_3)_4$]. | 17 | >99 | 43 |
| 13 | $RuCl_2(PGly)_2$ | 17 | >99 | - |
| 14 | [$RuCl(PGly)_2$]$BF_4$ | 1 | 99 | - |
| 15 | [$RuCl(PGly)_2$]$PF_6$ | 17 | >99 | - |
| 16 | [$RuCl(PGly)_2$]OTf | 17 | >99 | - |
| 17 | [$RuCl(PGly)_2$]$B(C_6F_5)_4$ | 0.5 | >99 | - |
| 18 | [$RuCl(PGly)_2$][$B(3,5\text{-}(CF_3)_2C_6H_3)_4$]. | 17 | >99 | - |
| 19 | [(*R*-binap)RuCl(*R*,*R*-dach)(MeCN)]$BF_4$ | 17 | >99 | 84 |
| 20 | [(*R*-binap)RuCl(*R*,*R*-dach)(pyr)]$BF_4$ | 17 | >99 | 83 |

[a] S:C:B = 830:1:18, *i*PrOH, r.t., $P_{H2}$=150 psi

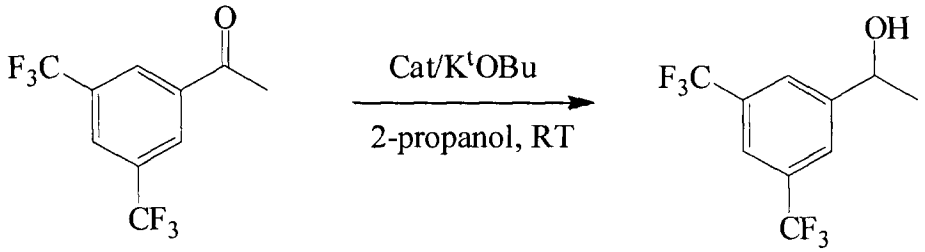
TABLE 3. RESULTS OF THE HYDROGENATION OF 4-FLUORO-ACETOPHENONE CATALYSED BY CATIONIC COMPLEXES OF RUTHENIUM.




| Entry | Complex | Time(h) | Conv.(%) | ee (%) |
|---|---|---|---|---|
| 1 | [RuCl(S-PPhos)(S-DAIPEN)]$BF_4$ | 4 | >99 | 73.6 |
| 2 | [RuCl(S-PPhos)(S-DAIPEN)]$B(C_6F_5)_4$ | 4 | >99 | 77 |
| 3 | [RuCl(S-xylylPPhos)(S-DAIPEN)]$BF_4$ | 4 | >99 | 99.1 |
| 4 | [RuCl(S-xylylPPhos)(S-DAIPEN)]$B(C_6F_5)_4$ | 4 | >99 | 99 |
| 5 | [RuCl(S-BINAP)(S-DAIPEN)]$BF_4$ | 4 | >99 | 75.4 |
| 6 | [RuCl(S-BINAP)(S-DAIPEN)]$B(C_6F_5)_4$ | 4 | >99 | 78.8 |

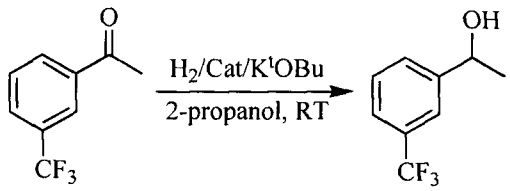
Substrate:Ru = 830, $P_{H2}$=160Psi

TABLE 4. RESULTS OF THE HYDROGENATION OF 3,5-BIS(TRIFLUOROMETHYL)-ACETOPHENONE CATALYSED BY CATIONIC COMPLEXES OF RUTHENIUM.



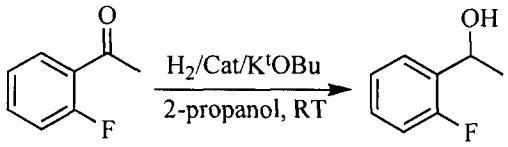

| Entry | Complex | Time(h) | Conv.(%) | ee (%) |
|---|---|---|---|---|
| 1 | [RuCl(S-PPhos)(S-DAIPEN)]$BF_4$ | 2 | >99 | 74 |
| 2 | [RuCl(S-PPhos)(S-DAIPEN)]$B(C_6F_5)_4$ | 2 | >99 | 75.5 |
| 3 | [RuCl(S-xylylPPhos)(S-DAIPEN)]$BF_4$ | 2 | >99 | 99.0 |
| 4 | [RuCl(S-xylylPPhos)(S-DAIPEN)]$B(C_6F_5)_4$ | 2 | >99 | 99.0 |
| 5 | [RuCl(S-BINAP)(S-DAIPEN)]$BF_4$ | 2 | >99 | 77 |
| 6 | [RuCl(S-BINAP)(S-DAIPEN)]$B(C_6F_5)_4$ | 2 | >99 | 78.7 |

TABLE 5. RESULTS OF THE HYDROGENATION OF 3-TRIFLUOROMETHYL-ACETOPHENONE CATALYSED BY CATIONIC COMPLEXES OF RUTHENIUM.



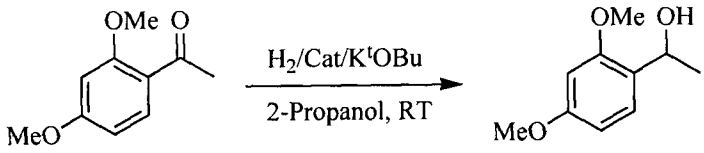

| entry | Cat. | Time(h) | Conv.(%) | ee (%) |
|---|---|---|---|---|
| 1 | [RuCl(S-PPhos,S-DAIPEN)]$BF_4$ | 1 | >99 | 76 |
| 2 | [RuCl(S-PPhos,S-DAIPEN)]$B(C_6F_5)_4$ | 1 | >99 | 81 |
| 3 | [RuCl(S-xylylPPhos,S-DAIPEN)]$BF_4$ | 1 | >99 | 98.7 |
| 4 | [RuCl(S-xylylPPhos,S-DAIPEN)]$B(C_6F_5)_4$ | 1 | >99 | 98.5 |
| 5 | [RuCl(S-BINAP,S-DAIPEN)]$BF_4$ | 1 | >99 | 76.5 |
| 6 | [RuCl(S-BINAP,S-DAIPEN)]$B(C_6F_5)_4$ | 1 | >99 | 76.7 |
| 7 | [$RuCl_2$(S)-PhanePhos,(R,R)DPEN] | 17 | >99 | 65.3 |
| 8 | [RuCl(S)-PhanePhos,(R,R)DPEN]$BF_4$ | 17 | >99 | 78.5 |
| 9 | [RuCl(S)PhanePhos,(R,R)DPEN]$B(C_6F_5)_4$ | 17 | >99 | 81.3 |
| 10 | [$RuCl_2$(S)-XylylPhanePhos,(R,R)DPEN] | 17 | >99 | 75.7 |
| 11 | [RuCl(S)-XylylPhanePhos,(R,R)DPEN] $BF_4$ | 17 | 97 | 71 |

TABLE 6. RESULTS OF THE HYDROGENATION OF 2-FLUORO-ACETOPHENONE CATALYSED BY CATIONIC COMPLEXES OF RUTHENIUM.



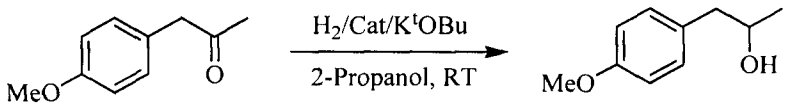

| entry | Cat . | Time(h) | Conv.(%) | ee (%) |
|---|---|---|---|---|
| 1 | [RuCl(S-PPhos,S-DAIPEN)]$BF_4$ | 2 | >99 | 80 |
| 2 | [RuCl(S-PPhos,S-DAIPEN)]$B(C_6F_5)_4$ | 2 | >99 | 80.3 |
| 3 | [RuCl(S-xylylPPhos,S-DAIPEN)]$BF_4$ | 2 | >99 | 95.3 |
| 4 | [RuCl(S-xylylPPhos,S-DAIPEN)]$B(C_6F_5)_4$ | 2 | >99 | 92.4 |
| 5 | [RuCl(S-BINAP,S-DAIPEN)]$BF_4$ | 2 | >99 | 80.7 |
| 6 | [RuCl(S-BINAP,S-DAIPEN)]$B(C_6F_5)_4$ | 2 | >99 | 84.6 |
| 7 | [$RuCl_2$(S)-PhanePhos,(R,R)DPEN] | 3 | 95 | 77.7 |
| 8 | [RuCl(S)-PhanePhos,(R,R)DPEN]$BF_4$ | 3 | 83 | 80 |
| 9 | [RuCl(S)PhanePhos,(R,R)DPEN]$B(C_6F_5)_4$ | 3 | 98 | 67 |
| 10 | [$RuCl_2$(S)-XylylPhanePhos,(R,R)DPEN] | 3 | 92 | 89.2 |
| 11 | [RuCl(S)-XylylPhanePhos,(R,R)DPEN] $BF_4$ | 3 | 63 | 82 |
| 12 | [RuCl(S)-XylylPhanePhos,(R,R)DPEN] $B(C_6F_5)_4$ | 3 | 93 | 87.3 |

TABLE 7. RESULTS OF THE HYDROGENATION OF 1-(2,4-DIMETHOXYPHENYL)ETHANONE CATALYZED BY RUTHENIUM COMPLEXES OF PHANEPHOS.



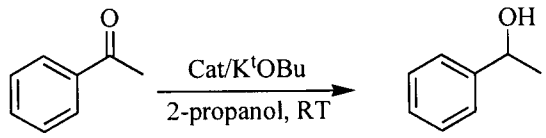

| Entry | Cat. | Time(h) | Conv.(%) | ee (%) |
|---|---|---|---|---|
| 1 | [$RuCl_2$(S)-PhanePhos,(R,R)DPEN] | 3 | >99 | 79.3 |
| 2 | [RuCl(S)-PhanePhos,(R,R)DPEN]$BF_4$ | 3 | >99 | 58.5 |
| 3 | [RuCl(S)PhanePhos,(R,R)DPEN]$B(C_6F_5)_4$ | 3 | >99 | 75 |
| 4 | [$RuCl_2$(S)-XylylPhanePhos,(R,R)DPEN] | 3 | >99 | 72 |
| 5 | [RuCl(S)-XylylPhanePhos,(R,R)DPEN] $BF_4$ | 3 | >99 | 47 |
| 6 | [RuCl(S)-XylylPhanePhos,(R,R)DPEN] $B(C_6F_5)_4$ | 3 | >99 | 57.7 |

TABLE 8. RESULTS OF THE HYDROGENATION OF 1-(4-METHOXYPHENYL)PROPAN-2-ONE CATALYZED BY RUTHENIUM COMPLEXES OF PHANEPHOS.




| Entry | Cat. | Time(h) | Conv.(%) | ee (%) |
|---|---|---|---|---|
| 1 | [$RuCl_2$(S)-PhanePhos,(R,R)DPEN] | 5 | 99 | 81 |
| 2 | [RuCl(S)-PhanePhos,(R,R)DPEN]$BF_4$ | 5 | >99 | 79 |
| 3 | [RuCl(S)PhanePhos,(R,R)DPEN]$B(C_6F_5)_4$ | 5 | >99 | 79 |
| 4 | [$RuCl_2$(S)-XylylPhanePhos,(R,R)DPEN] | 5 | >99 | 85 |
| 5 | [RuCl(S)-XylylPhanePhos,(R,R)DPEN] $BF_4$ | 5 | >88 | 75 |
| 6 | [RuCl(S)-XylylPhanePhos,(R,R)DPEN] $B(C_6F_5)_4$ | 5 | >99 | 78 |

TABLE 9. RESULTS OF THE HYDROGENATION OF ACETOPHENONE CATALYSED BY DICATIONIC COMPLEXES OF RUTHENIUM




| Entry | Complex | Time(h) | Conv.(%) | ee (%) |
|---|---|---|---|---|
| 1 | [Ru(R-binap)(R,R-cydn)][$BF_4$]$_2$ | 2 | >99 | 85 |
| 2 | [Ru(R-binap)($Ph_2PCH_2CH_2NH_2$)] [$BF_4$]$_2$ | 24 | 93 | 3 |
| 3 | [Ru(1R,2R-($Ph_2PC_6H_4CH_2NH$)$_2C_6H_{10}$)] [$BF_4$]$_2$ | 24 | 94 | 10 |

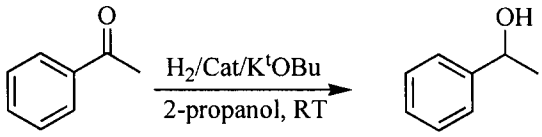
S/Cat =830

TABLE 10. RESULTS OF THE HYDROGENATION OF 2,3,3-TRIMETHYLINDOLENINE CATALYZED BY CATIONIC RUTHENIUM COMPLEXES.

| Entry | Cat | Time (h) | Conv. (%) | e.e. (%) |
|---|---|---|---|---|
| 1 | [(*R*-binap)RuCl(*R,R*-dach)]$BF_4$ | 17 | 57 | 30 |
| 2 | [(*R*-binap)RuCl(PGly)]$BF_4$ | 17 | 5 | 40 |
| 3 | [RuCl(PGly)$_2$]$BF_4$ | 17 | 62 | - |
| 4 | [RuCl(*R,R*-cyP$_2$N$_2$)]$BF_4$ | 17 | 16 | 76 |

[a] S:C:B = 180:1:26, *i*PrOH, r.t., 150 psi

TABLE 11. CATALYTIC HYDROGENATION OF ACETOPHENONE USING CATIONIC IRON COMPLEXES[A]

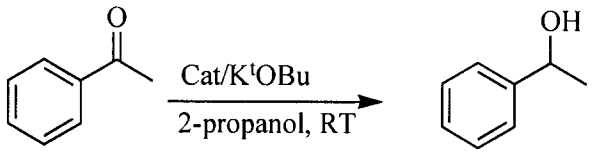



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| Entry | Catalyst C (Ex. #) | S:C:B | $T$ (°C) | $P_{H2}$ (atm) | Time (h) | Conv. (%) | ee (%) |
|---|---|---|---|---|---|---|---|
| 1 | 6(a) | 225:1:15 | 50 | 25 | 17 | 7 | 1 |
| 2 | 6(b) | 225:1:15 | 50 | 25 | 17 | 3 | 8 |
| 3 | 6(c) | 225:1:15 | 50 | 25 | 17 | 4 | 20 |
| 4 | 6(d) | 200:1:8 | 50 | 25 | 17 | 4 | 20 |
| 5 | 6(e) | 200:1:8 | 50 | 25 | 17 | 0 | - |
| 6 | 6(f) | 200:1:8 | 50 | 25 | 17 | 3 | - |
| 7 | 6(h) | 200:1:8 | 50 | 25 | 17 | 69 | 58 |
| 8 | 6(h) | 200:1:8 | 50 | 25 | 17 | 96 | 63 |
| 9 | 6(h) | 200:1:1 | 50 | 25 | 17 | 95 | 53 |

[a] S:C:B = 200:1:8, S= PhCOMe, C=catalyst, B = KO$^t$Bu; [S] = 0.36 M in 5 mL of *i*-PrOH.

TABLE 12: TRANSFER HYDROGENATION OF ACETOPHENONE USING CATIONIC IRON COMPLEXES[A]




| Entry | Catalyst (Example #) | S:C:B | T (°C) | Time (h) | Conv. (%) | e.e (%) |
|---|---|---|---|---|---|---|
| 1 | 6(a) | 200:1:10 | 25 | 19 | 0 | - |
| 2 | 6(a) | 200:1:10 | 80 | 19 | 0 | - |
| 3 | 6(e) | 200:1:10 | 80 | 19 | 0 | - |
| 4 | 6(f) | 200:1:10 | 25 | 19 | 0 | - |
| 5 | 6(f) | 200:1:10 | 80 | 18 | 19 | 22 |
| 6 | 6(g) | 200:1:10 | 25 | 3 | 12 | 78 |
| 7 | 6(h) | 200:1:10 | 25 | 3 | 6 | 60 |
| 8 | 6(h) | 200:1:10 | 80 | 3 | 3 | - |

[a] S= PhCOMe, C=catalyst, B = KO$^t$Bu; [S] = 0.36 M in 5 mL of *i*-PrOH.

WE CLAIM:

1. A compound selected from a compound of Formula I, II, III, IV and V:

$[M(P_2)(PN)X_q(LB)_n]^{r+}[Y^-]_r$ (I)

$[M(PN)_2X_q(LB)_n]^{r+}[Y^-]_r$ (II)

$[M(P)_m(N_2)X_q(LB)_n]^{r+}[Y^-]_r$ (III)

$[M(PNNP)X_q(LB)_n]^{r+}[Y^-]_r$ (IV) and

$[M(P_2)(N_2)X_q(LB)_n]^{r+}[Y^-]_r$ (V)

wherein

M is Fe, Ru or Os;

P is a monodentate ligand bonded to M via a phosphorus atom;

$P_2$ is a bidentate neutral ligand bonded to M via two phosphorus atoms;

$N_2$ is a bidentate neutral ligand bonded to M via two nitrogen atoms;

PN is a bidentate neutral ligand bonded to M via a phosphorus atom and a nitrogen atom;

PNNP is a tetradentate neutral ligand bonded to M via two phosphorus and two nitrogen atoms;

X is any anionic ligand;

LB is any neutral Lewis base;

Y is any non-coordinating anion;

n is 0, 1 or 2;

m is 1 or 2;

q is 0 or 1;

r is 1 or 2; and

$q + r = 2$.

2. The compound according to claim 1, wherein P is a monodentate phosphine ligand of the Formula (VI):

$PR^1R^2R^3$ (VI)

wherein

$R^1$, $R^2$ and $R^3$ are independently selected from $C_{6-18}$aryl, $C_{1-20}$alkyl and $C_{3-20}$cycloalkyl, each being optionally substituted with one to five substituents independently selected from $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, halo, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy and $C_{6-14}$aryl.

3. The compound according to claim 2, wherein $R^1$, $R^2$ and $R^3$ are independently selected from phenyl, $C_{1-6}$alkyl and $C_{3-10}$cycloalkyl, each being optionally substituted with one to three substituents independently selected from $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl, halo, $C_{1-4}$alkoxy and fluoro-substituted $C_{1-6}$alkoxy.

4. The compound according to claim 3, wherein $R^1$, $R^2$ and $R^3$ are all cyclohexyl, phenyl, xylyl or tolyl.

5. The compound according to claim 1, wherein $P_2$ is a bidentate bisphosphino ligand of the Formula (VII):

$R^4R^5P\text{-}Q^1\text{-}PR^6R^7$ (VII)

wherein

$R^4$, $R^5$, $R^6$ and $R^7$ are, independently, as defined for $R^1$, $R^2$ and $R^3$ in claim 2;

$Q^1$ is selected from unsubstituted or substituted $C_1$-$C_{10}$alkylene and unsubstituted or substituted $C_1$-$C_8$alkenylene where the substituents on $Q^1$ are independently selected from one or more of $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, halo, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy and unsubstituted or substituted $C_{6-14}$aryl; and/or

two substituents on $Q^1$ are joined together to form, including the carbon atoms to which they are attached, one or more unsubstituted or substituted 5-20-membered monocyclic, polycyclic, heterocyclic, carbocyclic, saturated, unsaturated or metallocenyl ring systems; where the term substituted with respect to the $Q^1$

substituents means that one or more of the available hydrogen atoms on the group are replaced with $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy, halo or $C_{6-14}$aryl; and

$Q^1$ is chiral or achiral.

6. The compound according to claim 5, wherein $R^4$, $R^5$, $R^6$ and $R^7$ are independently selected from phenyl, $C_{1-6}$alkyl and $C_{3-10}$cycloalkyl, each being optionally substituted with one to three substituents independently selected from $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl, halo, $C_{1-4}$alkoxy and fluoro-substituted $C_{1-4}$alkoxy;

$Q^1$ is selected from unsubstituted or substituted $C_1$-$C_8$alkylene where the substituents on $Q^1$ are independently selected from one to four $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl halo, $C_{1-4}$alkoxy, fluoro-substituted $C_{1-4}$alkoxy, unsubstituted and substituted phenyl and substituted and unsubstituted naphthyl, or two substituents are joined together to form, including the carbon atoms to which they are attached, one or more unsubstituted or substituted phenylene, cyclohexylene, naphthylene, pyridylene or ferrocenylene groups;

and $Q^1$ is chiral or achiral.

7. The compound according to claim 6, wherein $R^4$, $R^5$, $R^6$ and $R^7$ are all cyclohexyl, phenyl, xylyl or tolyl.

8. The compound according to claim 5, wherein the bis(phosphino) ligand is selected from:

2,2'-bis-(diphenylphosphino)-1,1'-binaphthyl (BINAP);

2,2'-bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl ($H_8$BINAP);

2,2'-bis-(diphenylphosphino)-6,6'-dimethyl-1,1'-binaphthyl (6MeBINAP);

2,2'-bis-(di-p-tolylphosphino)-1-,1'-binaphthyl (Tol-BINAP);

2,2'-bis[bis(3-methylphenyl)phosphino]-1,1'-binaphthyl;

2,2'-bis[bis(3,5-di-tert-butylphenyl)phosphino]-1,1'-binaphthyl;

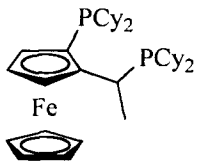
2,2'-bis[bis(4-tert-butylphenyl)phosphino]-1,1'-binaphthyl;

2,2'-bis[bis(3,5-dimethylphenyl)phosphino]-1,1'-binaphthyl (Xyl-BINAP);

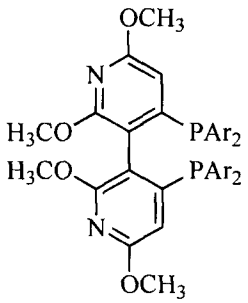
2,2'-bis[bis(3,5-dimethyl-4-methoxyphenyl)phosphino]-1,1'-binaphthyl (Dmanyl-BINAP);

2,2'-bis[bis-(3,5-dimethylphenyl)phosphino]-6,6'-dimethyl-1,1'-binaphthyl (Xyl-6MeBINAP);

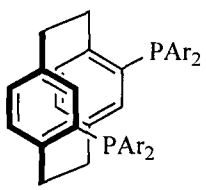
3,3'-bis-(diphenylphosphanyl)-13,13'-dimethyl-12,13,14,15,16,17,12',13',14',15',16',17'-dodecahydro-11H,11'H-[4,4']bi[cyclopenta[a]phenanthrenyl];




wherein Cy is $C_{5-8}$cycloalkyl;




where Ar is phenyl (PPhos), xylyl (XylPPhos) or tolyl (TolPPhos);




where Ar is phenyl (PhanePhos), xylyl (XylPhanePhos) or tolyl (TolPhanePhos); and optical isomers thereof and mixtures of optical isomers in any ratio.

9. The compound according to claim 1, wherein PN is a ligand of the Formula (VIII):

$R^8R^9P\text{-}Q^2\text{-}NR^{10}R^{11}$ (VIII)

wherein $R^8$ and $R^9$ are, independently as defined for $R^1$-$R^3$ in claim 2;

$Q^2$ is as defined for $Q^1$ in claim 5; and

$R^{10}$ and $R^{11}$ are independently selected from H, $C_{6-18}$aryl, $C_{1-20}$alkyl and $C_{3-10}$cycloalkyl, each being optionally substituted with one to five substituents independently selected from $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl halo, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy and $C_{6-14}$aryl, or

$R^{10}$ and $R^{11}$ are joined to form, together with the nitrogen atom to which they are attached, a saturated, unsaturated or aromatic, monocyclic or polycyclic, substituted or unsubstituted ring system containing from 3 to 14 atoms, or

one of $R^{10}$ or $R^{11}$ are joined with a substituent on $Q^2$ to form, together with the nitrogen atom to which $R^{10}$ and $R^{11}$ is attached, a 4- to 10-membered saturated, unsaturated or aromatic, monocyclic or bicyclic ring system, where if the nitrogen atom is part of aromatic ring or is bonded to an adjacent atom via a double bond, the other of $R^{10}$ and $R^{11}$ is non-existent.

10. The compound according to claim 9, wherein $R^8$ and $R^9$ are independently selected from phenyl, $C_{1-6}$alkyl and fluoro-substituted $C_{1-6}$alkyl, with the phenyl being optionally substituted with one to five substituents independently selected from $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl halo, $C_{1-4}$alkoxy and fluoro-substituted $C_{1-4}$alkoxy;

$Q^2$ is selected from unsubstituted or substituted $C_1$-$C_8$alkenylene where the substituents on $Q^2$ are independently selected from one to four of $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, halo, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy and unsubstituted or substituted phenyl; and/or

adjacent substituents on $Q^2$ are joined together to form, including the carbon atoms to which they are attached, one or more unsubstituted or substituted phenylene, naphthylene or ferrocenylene ring systems or ;

the term substituted with respect to the $Q^2$ substituents means that one or more of the available hydrogen atoms on the group are replaced with $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy, halo or $C_{6-14}$aryl; and

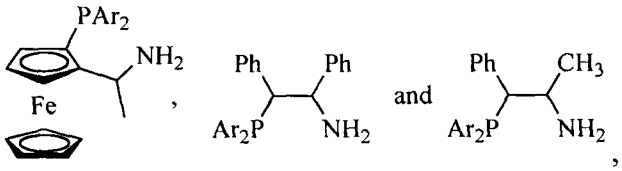
$Q^2$ is chiral or achiral.

11. The compound according to claim 10, wherein $R^4$, $R^5$, $R^6$ and $R^7$ are all phenyl, tolyl or xylyl.

12. The compound according to claim 10, wherein $R^{10}$ and $R^{11}$ and both H or one of $R^{10}$ or $R^{11}$ is joined with a substituent on $Q^2$ to form, together with the nitrogen atom to which $R^{10}$ and $R^{11}$ is attached, a substituted or unsubstituted pyridine ring and the other of one of $R^{10}$ or $R^{11}$ is not present.

13. The compound according to claim 9, wherein PN is selected from:

$Ph_2PCH_2CH_2NH_2$ (PGly); and




wherein Ar is selected from Ph, tolyl and xylyl; and

optical isomers thereof and mixtures of optical isomers in any ratio.

14. The compound according to claim 1, wherein PNNP is a tetradentate diaminodiphosphine of the formula (IXa) or a diiminodiphosphine ligand of the Formula (IXb) :

$R^{12}R^{13}P\text{-}Q^3\text{-}NR^{14}\text{-}Q^4\text{-}NR^{15}\text{-}Q^5\text{-}PR^{16}R^{17}$ (IXa)

$R^{12}R^{13}P\text{-}Q^3{=}N\text{-}Q^4\text{-}N{=}Q^5\text{-}PR^{16}R^{17}$ (IXb)

wherein $R^{12}$, $R^{13}$, $R^{16}$ and $R^{17}$ are independently as defined for $R^1$-$R^3$ in claim 2;

$R^{14}$ and $R^{15}$ are independently as defined for $R^{10}$ and $R^{11}$ in claim 9; and

$Q^3$, $Q^4$ and $Q^5$ are independently as defined for $Q^1$ in claim 5.

15. The compound according to claim 14, wherein $R^{12}$, $R^{13}$, $R^{16}$ and $R^{17}$ are independently selected from phenyl, $C_{1-6}$alkyl and $C_{3-10}$cycloalkyl, each being optionally substituted with one to five substituents independently selected from $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl, halo, $C_{1-4}$alkoxy and fluoro-substituted $C_{1-6}$alkoxy;

$Q^3$, $Q^4$ and $Q^5$ are independently selected from unsubstituted or substituted $C_1$-$C_8$alkylene and unsubstituted or substituted $C_1$-$C_8$alkenylene, where the substituents on $Q^3$, $Q^4$ and $Q^5$ are independently selected from one to four $C_{1-4}$alkyl, fluoro-substituted $C_{1-4}$alkyl, halo, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy, unsubstituted and substituted phenyl and substituted and unsubstituted naphthyl; and/or

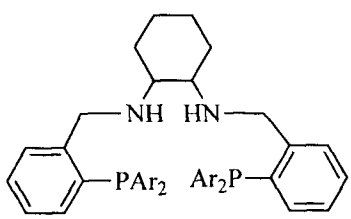
two substituents on $Q^3$, $Q^4$ and $Q^5$ are joined together to form, including the carbon atoms to which they are attached, one or more unsubstituted or substituted phenyl, cyclohexyl, naphthyl or ferrocenyl groups;

the term substituted with respect to the subtituents on $Q^3$, $Q^4$ and $Q^5$ means that one or more of the available hydrogen atoms on the group are replaced with $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy, halo or $C_{6-14}$aryl; and

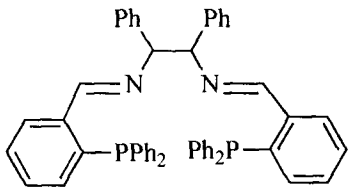
$Q^3$, $Q^4$ and $Q^5$ are chiral or achiral.

16. The compound according to claim 15, wherein $R^{12}$, $R^{13}$, $R^{16}$ and $R^{17}$ are all phenyl, tolyl or xylyl.

17. The compound according to claim 14, wherein PNNP is selected from:



wherein Ar is phenyl (DPPcydn), tolyl (di(p-tolyl)PPcydn) and xylyl (di(3,5xylyl)PPcydn);




(dpenPPh$_2$N$_2$); and

optical isomers thereof and mixtures of optical isomers in any ratio.

18. The compound according to claim 1, wherein $N_2$ is a bidentate diamine ligand of the Formula (X):

$$R^{18}R^{19}N\text{-}Q^6\text{-}NR^{20}R^{21} \quad (X)$$

wherein $R^{18}$, $R^{19}$, $R^{20}$ and $R^{21}$ are independently as defined for $R^{10}$ and $R^{11}$ in claim 9; or

one of $R^{18}$ or $R^{19}$ and/or $R^{20}$ or $R^{21}$ are joined with a substituent on $Q^6$ to form, together with the nitrogen atom to which $R^{18}$, $R^{19}$, $R^{20}$ or $R^{21}$ is attached, a 4- to 10-membered saturated, unsaturated or aromatic, monocyclic or bicyclic ring system, where if the nitrogen atom is part of aromatic ring or is bonded to an adjacent atom via a double bond, the other of $R^{18}$ or $R^{19}$ and/or $R^{20}$ or $R^{21}$ is not present;

the term substituted with respect to the subtituents on $Q^6$ means that one or more of the available hydrogen atoms on the group are replaced with $C_{1\text{-}6}$alkyl, fluoro-substituted $C_{1\text{-}6}$alkyl, $C_{1\text{-}6}$alkoxy, fluoro-substituted $C_{1\text{-}6}$alkoxy, halo or $C_{6\text{-}14}$aryl; and

$Q^6$ is as defined for $Q^1$ in claim 5.

19. The compound according to claim 18, wherein

$R^{18}$, $R^{19}$, $R^{20}$ and $R^{21}$ are all H;

$Q^6$ is selected from unsubstituted or substituted $C_1$-$C_8$alkenylene where the substituents on $Q^6$ are independently selected from one to four of $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl, halo, $C_{1-6}$alkoxy, fluoro-substituted $C_{1-6}$alkoxy and unsubstituted or substituted phenyl; and/or

two substituents on $Q^6$ are joined together to form, including the carbon atoms to which they are attached, one or more unsubstituted or substituted phenyl, naphthyl or ferrocenyl ring systems; and

$Q^6$ is chiral or achiral.

20. The compound according to claim 18, wherein one of $R^{18}$ or $R^{19}$ or $R^{20}$ or $R^{21}$ are joined with a substituent on $Q^6$ to form, together with the nitrogen atom to which $R^{18}$, $R^{19}$, $R^{20}$ or $R^{21}$ is attached, a pyridine ring and the other of one of $R^{18}$ or $R^{19}$ and/or $R^{20}$ or $R^{21}$ is not present.

21. The compound according to claim 18, wherein $N_2$ is selected from:

methylenediamine;

ethylenediamine;

1,2-diaminopropane;

1,3-diaminopropane;

1,4-diaminobutane;

2,3-diaminobutane;

1,2-cyclopentanediamine;

1,2-cyclohexanediamine;

1,1-diphenylethylenediamine (DPEN);

1,1-di(p-methoxyphenyl)ethylenediamine;

1,1-di(3,5-dimethoxyphenyl)ethylenediamine;

1,1-dinaphthylethylenediamine;

1,2-cycloheptanediamine;

2,3-dimethylbutanediamine;

1-methyl-2,2-diphenylethylenediamine (DACH or CYDN);

1-isobutyl-2,2-diphenylethylenediamine;

1-isopropyl-2,2-diphenylethylenediamine;

1-benzyl-2,2-diphenylethylen-ediamine;

1-methyl-2,2-di(p-methoxyphenyl)ethylenediamine (DAMEN);

1-isobutyl-2,2-di(p-methoxyphenyl)-ethylenediamine (DAIBEN);

1-isopropyl-2,2-di(p-methoxyphenyl)ethylenediamine (DAIPEN);

1-benzyl-2,2-di(p-methoxyphenyl)ethylenediamine;

1-methyl-2,2-di(3,5-dimethoxyphenyl)ethylenediamine;

1-isopropyl-2,2-di(3,5-dimethoxyphenyl)ethylenediamine,

1-isobutyl-2,2-di(3,5-dimethoxy-phenyl)ethylenediamine;

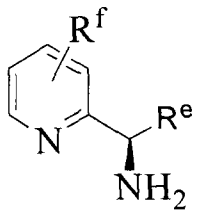
1-benzyl-2,2-di(3,5-dimethoxyphenyl)ethylenediamine;

1-methyl-2,2-dinaphthylethylenediamine;

1-isobutyl-2,2-dinaphthylethylene-diamine;

1-isopropyl-2,2-dinaphthylethylenediamine;

1-benzyl-2,2-dinaphthylethylenediamine;




wherein $R^e$ is H, $C_{1-6}$alkyl, fluoro-substituted $C_{1-6}$alkyl or aryl and $R^f$ is H, halo, $C_{1-6}$alkyl, fluoro-substituted-$C_{1-6}$alkyl, $C_{2-6}$alkenyl, $C_{2-6}$alkynyl, $C_{3-7}$cycloalkyl, $C_{1-6}$alkoxy, fluoro-substituted-$C_{1-6}$alkoxy or $C_{6-14}$aryl; and

optical isomers thereof and mixtures of optical isomers in any ratio.

22. The compound according to any one of claims 1-21, wherein X is selected from halo, $C_{1-6}$alkoxy, carboxylate, sulfonates and nitrates.

23. The compound according to any one of claims 1-22, wherein LB is selected from acetonitrile, DMF and pyridine.

24. The compound according to any one of claims 1-23, wherein Y is selected from:

a) OTf,

b) $BF_4$,

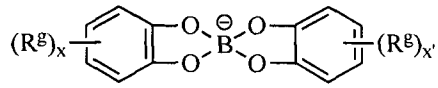
c) $PF_6$,

d) $B(C_{1-6}alkyl)_4$,

e) $B(fluoro\text{-}substituted\text{-}C_{1-6}alkyl)_4$,

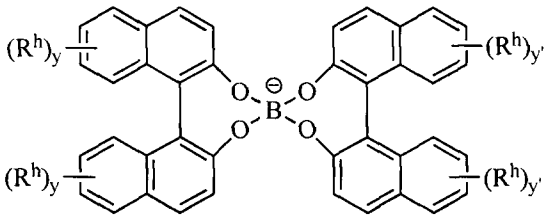
f) $B(C_{6-18}aryl)_4$, wherein aryl is unsubstituted or substituted 1-5 times with fluoro, $C_{1-4}$alkyl or fluoro-substituted $C_{1-4}$alkyl,

g)



, $R^g$ is independently halo, $C_{1-4}$alkyl or fluoro-substituted-$C_{1-4}$alkyl and x and x' are independently an integer between 1 and 4,

h)



, wherein $R^h$ is independently halo, $C_{1-4}$alkyl or fluoro-substituted-$C_{1-4}$alkyl and y and y' are independently an integer between 1 and 6,

i) $Al(C_{1-6}alkyl)_4$,

j) $Al(fluoro\text{-}substituted\text{-}C_{1-6}alkyl)_4$,

k) $Al(C_{6-18}aryl)_4$, wherein aryl is unsubstituted or substituted 1-5 times with fluoro, $C_{1-4}$alkyl or fluoro-substituted $C_{1-4}$alkyl,

l) $Al(\text{-}O\text{-}C_{1-6}alkyl)_4$,

m) $Al(\text{-}O\text{-}fluoro\text{-}substituted\text{-}C_{1-6}alkyl)_4$

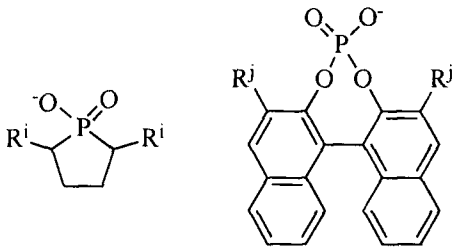
n) $Al(\text{-}O\text{-}C_{6-18}aryl)_4$, wherein aryl is unsubstituted or substituted 1-5 times with fluoro, $C_{1-4}$alkyl or fluoro-substituted $C_{1-4}$alkyl

o) a carborane,

p) a bromocarborane; and

q) a phosphate.

25. The compound according to claim 24, wherein the phosphate anion is of the formula



wherein $R^i$ and $R^j$ are independently selected from halo, $C_{1-4}$alkyl, fluoro-substituted-$C_{1-4}$alkyl or $C_{6-18}$aryl.

26. The compound according to claim 24, wherein the carborane is $CB_{11}H_{12}$.

27. The compound according to claim 24, wherein the bromocarborane is $CB_{11}H_6Br_6$.

28. The compound according to any one of claims 24-27, wherein Y is chiral.

29. A process for preparing a compound of claim 1, comprising combining a compound of the formula

$M(P_2)(PN)X_2$ (XI)

$M(PN)_2X_2$ (XII)

$M(P)_m(N_2)X_2$ (XIII)

$M(PNNP)X_2$ (XIV) or

$M(P_2)(N_2)X_2$ (XV)

wherein M, $P_2$, PN, P, PNNP, $P_2$ and X are as defined in claim 1, with one or two molar equivalents of a an anion abstracting agent and optionally a non- or weakly-

coordinating Lewis Base, and reacting under conditions to form the compound of the disclosure and optionally isolating the compound.

30. A process for preparing a compound of claim 1, comprising combining a precursor metal compound with one or two molar equivalents of an anion abstracting agent, and optionally a Lewis Base and reacting under conditions to form a cationic or dicationic precursor metal compound and combining the cationic or dicationic precursor metal compound with one or more P, $P_2$, $N_2$, PN, or PNNP ligands, as defined in claim 1, and optionally a non- or weakly-coordinating Lewis Base, under conditions to form the compound and optionally isolating the compound.

31. The process according to claim 30, wherein the precursor metal compound is of the formula $[MX_2(p\text{-ligand})]_2$ or $MX_2$(ligand), wherein M and X are as defined in claim 1 and ligand is any displaceable ligand.

32. The process according to claim 31, wherein the displaceable ligand is *p*-cymene, benzene, cyclooctadiene (COD) or norbornadiene (NBD) and M is a metal selected from Fe, Ru and Os.

33. The process according to claim 32, wherein the displaceable ligand is *p*-cymene of NBD and M is Ru/.

34. The process according to claim 30, wherein the precursor metal compound is of the formula $MX_2(P_2)(LB)_n$, wherein M, X, $P_2$ and LB are as defined in claim 1 and n is 1 or 2.

35. The process according to claim 34, wherein ($P_2$) is BINAP and LB is DMF or pyridine.

36. The process according to any one of claims 29-35, wherein the anion abstracting agent is a salt of a non-coordinating counter anion Y, wherein Y is as defined in any one of claims 24-28.

37. A method for catalyzing a synthetic organic reaction comprising combining starting materials for the reaction with a compound according to any one of claims 1-28 under conditions for performing the reaction.

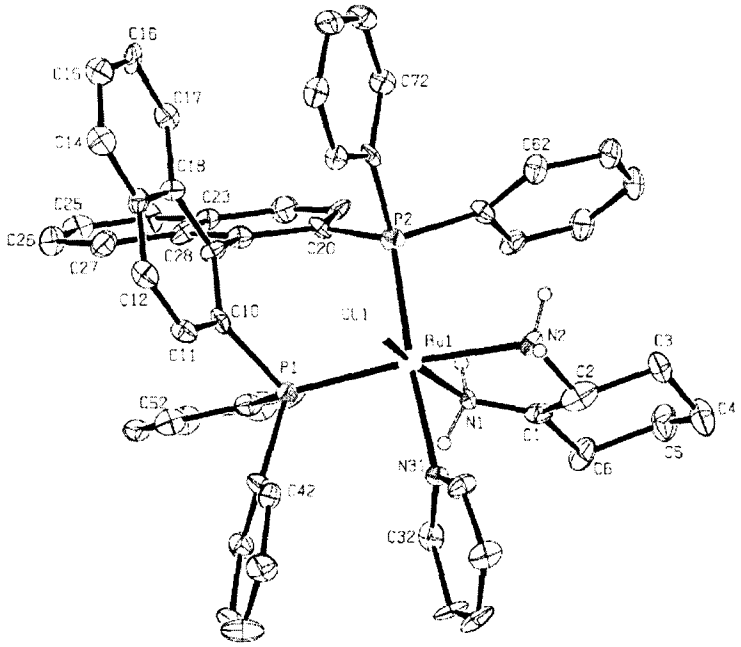
38. The method according to claim 37, wherein the synthetic organic reaction is selected from hydrogenation, transfer hydrogenation, hydroformylation, hydrosilylation, hydroboration, hydroamination, hydrovinylation, hydroarylation, hydration, oxidation, epoxidation, reduction, C-C and C-X bond formation, functional group interconversion, kinetic resolution, dynamic kinetic resolution, cycloaddition, Diels-Alder, retro-Diels-Alder, sigmatropic rearrangement, electrocyclic reactions, ring-opening and/or ring-closing olefin metathesis, carbonylation and aziridination.

39. The method according to claim 38, wherein the C-C and C-X bond formation reaction is selected from Heck, Suzuki-Miyaura, Negishi, Buchwald-Hartwig Amination, α-Ketone Arylation, N-Aryl Amination, Murahashi, Kumada, Negishi and Stille reactions.

40. The method according to claim 38, wherein the reaction is hydrogenation or transfer hydrogenation

41. The method according to any one of claims 38-40 wherein the reaction is regioselective, chemoselective, stereoselective or diastereoselective.

FIGURE 1


C16
C15
C17
C14
C18
C25
C23
C26
C27
C28
C20
C72
C62
P2
C12
C10
C11
Cl1
Ru1
N2
O3
P1
C2
C52
N1
C1
C4
C5
C6
N31
C42
C32

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/CA2008/001905

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C07F 15/00*** (2006.01) , ***B01J 23/74*** (2006.01) , ***C07C 211/65*** (2006.01) , ***C07F 15/02*** (2006.01) , ***C07F 9/50*** (2006.01)
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)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
STN (structure); SCOPUS (Ru, ruthenium, Fe, iron, Os, osmium, diphosphine*, bisphosphine*, bis*phosphine*, BINAP, NCA, non*coordinating, anion, PF6, BF4, borate*, cationic, aminophosphine*, iminophosphine*, phosphino*amine*, phosphino*imine*, diimin*, bisimine*, diamine*, bisamino, dpen, dach, cydn, *diamino*, *diamine, monophosphine, triphenylphosphine, triarylphosphine*, tristolylphosphine, PPh3, amino*pyridine*, damen, daiben, daipen, PNNP, P2N2, tetradentate, *PPcydn)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br>Y | Gimeno et al., *Journal of Organometallic Chemistry* **2002**, *663*, pages 204-212.<br>Introduction page 204; compounds 3 and 9, pages 209, 211<br>(Group 1 inventions) | 1-7, 9-11, 14-27, 29, 30, 36-41<br>28 |
| X | Schutte et al., *Inorganic Chemistry* **1997**, *36*, pages 5809-5817.<br>compounds 6a, 6b, 6c, pages 5810-5811<br>(Group 1 inventions) | 1-7, 9-12, 14-27, 29, 36 |
| A | CA 2,422,029 (Rautenstrauch et al.)<br>21 March 2002 (21-03-2002)<br>whole document<br>(Group 1 inventions) | 1-27, 37-41 |

[X] Further documents are listed in the continuation of Box C. [X] 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 |
|---|---|
| 6 February 2009 (06-02-2009) | 18 February 2009 (18-02-2009) |

| Name and mailing address of the ISA/CA | Authorized officer |
|---|---|
| Canadian Intellectual Property Office<br>Place du Portage I, C114 - 1st Floor, Box PCT<br>50 Victoria Street<br>Gatineau, Quebec K1A 0C9<br>Facsimile No.: 001-819-953-2476 | Samantha Drouin 819- 934-2324 |

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/CA2008/001905

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the 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. [ ] Claim Nos. :
because they relate to subject matter not required to be searched by this Authority, namely :

2. [ ] Claim 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. [ ] Claim 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 supplemental sheet.

1. [X] 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 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 claim 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 claim Nos. :

**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.

**Box No. IV** **Text of the abstract (Continuation of item 5 of the first sheet)**

The present disclosure includes cationic complexes of iron, ruthenium, and osmium, and their use as catalysts in organic synthesis transformations including the hydrogenation of unsaturated compounds. The complexes are represented by the following formulae I, II, III, IV, and V, wherein M is Fe, Ru or Os, P is a monodentate ligand with a phosphorus donor atom, $P_2$ is a bidentate neutral ligand with two phosphorus donor atoms, $N_2$ is a bidentate neutral ligand with two nitrogen donor atoms, PN is a bidentate neutral ligand with phosphorus and nitrogen donor atoms, PNNP is a tetradentate neutral ligand bonded to M via two phosphorus and two nitrogen atoms, X is any anionic ligand, LB is any neutral Lewis base, Y is any non-coordinating anion, n is 0, 1, or 2, m is 1 or 2, q is 0 or 1, r is 1 or 2 and q + r = 2.

$[M(P_2)(PN)X_q(LB)_n]^{r+}[Y^-]_r$ (I)

$[M(PN)_2X_q(LB)_n]^{r+}[Y^-]_r$ (II)

$[M(P)_m(N_2)X_q(LB)_n]^{r+}[Y^-]_r$ (III)

$[M(PNNP)X_q(LB)_n]^{r+}[Y^-]_r$ (IV) and

$[M(P_2)(N_2)X_q(LB)_n]^{r+}[Y^-]_r$ (V)

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br>Y | Del Zotto et al., *Inorganica Chimica Acta* **2000**, *299*, pages 180-191.<br>Introduction pages 180-181; compounds 3, 5, 8–13, 17, 18<br><br>(Group 2 inventions) | 1-12, 14-27, 37-40<br>28 |
| X | Del Zotto et al, *J. Chem. Soc. Dalton Trans.* **1994**, pages 2257-2264.<br>compounds 4 and 7-16<br><br>(Group 2 inventions) | 1-12, 14-27, 30, 31, 36 |
| X | Costella et al., *J. Chem. Soc. Dalton Trans.* **1993**, pages 3001-3008.<br>compounds 5a, 5b, 5c, 6a, 6b, 7c<br><br>(Group 2 inventions) | 1-12, 14-27, 29, 36 |
| X | Shen et al., *Inorganica Chimica Acta* **1998**, *268*, pages 69-76.<br>compounds 4, 6a, 6b, 6c, 7, 8, 9<br><br>(Group 2 inventions) | 1-12, 14-27, 29, 36 |
| X<br>A | "Ruthenium (II) Complexes bearing Bis(phosphine) and ß-Aminophosphine Ligands and their Application to homogeneous >C=O Reduction". Kühnlein, C. Doctoral thesis. 14 December 2005. Universität Erlange-Nürnberg.<br>See chapter 9, compound 22 (Group 2 inventions)<br>Whole document (Groups 1 and 2 inventions) | 1-12, 14-27, 29, 36<br>1-27, 29, 37-41 |
| X | Sullivan et al., *Organometallics* **1984**, *3*, pages 1241-1251.<br>whole document<br><br>(Groups 3 and 5 inventions) | 1-18, 20, 22-27, 29-31, 36 |
| X | Sullivan et al., *Inorganic Chemistry* **1978**, *17*, pages 3334-3341.<br>whole document<br><br>(Groups 3 and 5 inventions) | 1-18, 20, 22-27, 29, 30, 36 |
| Y | Clapham et al., *Coordination Chemistry Reviews* **2004**, *248*, pages 2201-2237.<br>Schemes 6, 9 (pages 2215, 2219)<br><br>(Groups 3, 4 and 5 inventions) | 1-27, 29, 36-41 |



**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/CA2008/001905

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|---|---|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| Y | WO 05/105819 (Baratta et al.)<br>10 November 2005 (10-11-2005)<br>whole document<br><br>(Groups 3 and 5 inventions) | 1-27, 29, 36-41 |
| X<br>Y | Stoop et al., *Organometallics* **2000**, *19*, pages 4117-4126.<br>compounds 3a, 3b, 5b, 5c, 6; Tables 2-4; page 4126<br><br>(Group 4 inventions) | 1-27, 29, 36-39, 41<br>28 |
| X<br>Y | "Novel Iron(II) Complexes with Tetradentate P-N-N-P Donor Ligands and their Application in Hydrogenation of Ketones", Sui-Seng et al., INP 0159; Inorganic Chemistry Poster (abstract)<br>90th Canadian Chemistry Conference, Winnipeg, Manitoba, presented 27 May 2007 (27-05-2007)<br><br>(Group 4 inventions) | 1-13, 18-27, 37-40<br>28 |
| X | WO 06/106484 (Saudan et al.)<br>12 October 2006 (12-10-2006)<br>page 4, line 24 to page 5, line 3; page 9, line 18 to page 10, line 2; claims<br><br>(Group 4 inventions) | 1-27, 29, 36-41 |
| X<br>Y | Barthazy et al., *Organometallics* **2001**, *20*, pages 3472-3477.<br>compound 4; Tables 1, 2<br><br>(Group 4 inventions) | 1-16, 18-27, 29, 36-38, 41<br>28 |
| X<br>Y | Bonaccorsi et al., *Tetrahedron: Asymmetry* **2003**, *14*, pages 845-854.<br>compounds 4a, 5a, 5b, 6a, 6b, 7b; Tables 2-4<br><br>(Group 4 inventions) | 1-16, 18-27, 29, 36-39, 41<br>28 |
| X<br>Y | Bachmann et al., *Organometallics* **2001**, *20*, pages 2102-2108.<br>compound 3a; Tables 1, 2<br><br>(Group 4 inventions) | 1-16, 18-27, 29, 36-39, 41<br>28 |
| X<br>Y | Wong et al. *European Journal of Inorganic Chemistry* **2003**, pages 3539-3546.<br>compounds 1, 2, 3, 4; Tables 2-5<br><br>(Group 4 inventions) | 1-27, 29, 36-39, 41<br>28 |



**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/CA2008/001905

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
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| | Bonaccorsi et al. *Current Organic Chemistry* **2006**, *10*, pages 225-240. | |
| X<br>Y | whole document<br><br>(Group 4 inventions) | 1-16, 18-27, 29, 36-39, 41<br>28 |
| | Gao et al., *Polyhedron* **1996**, *15*, pages 1241-1251. | |
| X | compound (VI)<br><br>(Group 4 inventions) | 1-16, 18-27 |
| | Sui-Seng et al., *Angew. Chem. Int. Ed.* **2008**, *47*, pages 940-943. 20 December 2007 (20-12-2007) | |
| P, X<br>P, Y | compounds 1, 2, 3, 4; Table 1<br><br>(Group 4 inventions) | 1-16, 18-27, 37-41<br>28 |
| | Hamilton et al., *J. Am. Chem. Soc.* **2006**, *128*, pages 13700-13701, and Supporting Information. | |
| X<br>Y | whole document<br><br>(Group 5 inventions) | 1-27, 30-32, 36-41<br>28 |
| | Jing et al., *European Journal of Organic Chemistry* **2006**, pages 3606-3616. | |
| X | compounds 3a, 3b, 3c, 3d; Tables 2 and 4<br><br>(Group 5 inventions) | 1-27, 37-41 |
| | Yam et al., *J. Chem. Soc. Dalton Trans.* **1997**, pages 2335-2339. | |
| X | compounds 1, 2, 3, 4<br><br>(Group 5 inventions) | 1-7, 9-18, 20, 22-27, 30, 31, 36 |
| | Bickley et al., *Dalton Trans.* **2003**, pages 4663-4668. | |
| X | compounds 5a, 6a, 6b<br><br>(Group 5 inventions) | 1-7, 9-19, 22-27, 30, 34, 36 |



**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/CA2008/001905

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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| | Araujo et al., *Organometallics* **2005**, *24*, pages 6159-6168. | |
| X | compounds 1b, 2b, 3b, 4b: Table 3 | 1-7, 9-18, 20, 22-27, 29, 36-41 |
| Y | | 28 |
| | (Group 5 inventions) | |
| | Hamilton et al. *Science* **2007**, *317*, pages 496-499.<br>27 July 2007 (27-07-2007) | |
| Y | whole document | 28 |
| | (Groups 1-5 inventions) | |

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Continuation of Box No. III

The application is directed to multiple inventions as follows:

**Group 1.** Claims 1-41 (in part) featuring ionic compounds of Formula (I), processes for making said compounds, and the use of said compounds in methods of catalyzing synthetic organic reactions, wherein the cationic portion of Formula (I) is a complex of an iron-group metal comprising a ligand ($P_2$), which is a bidentate neutral ligand bonded to M via two phosphorus atoms, and a ligand (PN), which is a bidentate neutral ligand bonded to the metal via a phosphorus atom and a nitrogen atom.

**Group 2.** Claims 1-41 (in part) featuring ionic compounds of Formula (II), processes for making said compounds, and the use of said compounds in methods of catalyzing synthetic organic reactions, wherein the cationic portion of Formula (II) is a complex of an iron-group metal comprising two ligands (PN), which are bidentate neutral ligands bonded to M via a phosphorus atom and a nitrogen atom.

**Group 3.** Claims 1-41 (in part) featuring ionic compounds of Formula (III), processes for making said compounds, and the use of said compounds in methods of catalyzing synthetic organic reactions, wherein the cationic portion of Formula (III) is a complex of an iron-group metal comprising a ligand ($N_2$), which is a bidentate neutral ligand bonded to M via two nitrogen atoms, and one or two ligands (P), which are each monodentate and bonded to the metal via a phosphorus atom.

**Group 4.** Claims 1-41 (in part) featuring ionic compounds of Formula (IV), processes for making said compounds, and the use of said compounds in methods of catalyzing synthetic organic reactions, wherein the cationic portion of Formula (IV) is a complex of an iron-group metal comprising a ligand (PNNP), which is a tetradentate neutral ligand bonded to M via two phosphorus atoms and two nitrogen atoms.

**Group 5.** Claims 1-41 (in part) featuring ionic compounds of Formula (V), processes for making said compounds, and the use of said compounds in methods of catalyzing synthetic organic reactions, wherein the cationic portion of Formula (V) is a complex of an iron-group metal comprising a ligand ($P_2$), which is a bidentate neutral ligand bonded to M via two phosphorus atoms, and a ligand ($N_2$), which is a bidentate neutral ligand bonded to the metal via two nitrogen atoms.

The technical feature that is common to all claims is the combination of the following structural elements in the definition of the complex: (1) the central metal is an iron-group metal, (2) the complex is cationic and includes a non-coordinating anion, (3) there is at least one phosphorus donor-atom in the ligand sphere, (4) the complex includes at least one chelating ligand comprising nitrogen as a donor atom. This combination of structural elements is known; the documents listed in the present search report illustrate the state of the art. Since the linking technical feature of the claims is known, it cannot be relied upon to represent a unifying inventive concept for the claims.