

HYDROGENATION AND DEHYDROGENATION CATALYST, AND METHODS OF MAKING AND USING THE SAME

FIELD OF THE INVENTION

[0001] The present invention pertains to catalysts. More specifically, the present invention pertains to catalysts useful in hydrogenation and dehydrogenation reactions.

INTRODUCTION

[0002] Reduction of esters is one of the most fundamental organic reactions and is useful for synthesis of a variety of useful organic alcohols. The reduction of esters is typically accomplished using main-group hydride reagents, such as LiAlH_4 , or using molecular hydrogen. The use of hydride reducing reagents is inconvenient and expensive, particularly on a large scale; furthermore, this approach generates large amounts of chemical waste. The hydride reduction method can also be dangerously exothermic at the stage of quenching and it can be difficult to control. The catalytic reduction of esters under hydrogen gas is, in all respects, a very attractive 'green' alternative to the classical hydride reduction.

[0003] A key aspect of the ester reduction with molecular hydrogen is the catalytic system utilized in the process that can rapidly bind and split molecular hydrogen to give a transition-metal hydride. The development of highly efficient and useful catalysts and catalytic systems for hydrogenation of lactones, esters, oils, and fats is an important need in chemistry. Particularly, developing hydrogenation processes operating in the temperature range of 20 to 100°C using less than 1000 ppm (0.1 mol%) catalyst under relatively low H_2 pressure (1 – 50 bar) is highly desirable. Among the few catalysts and catalytic systems capable of converting esters and lactones into alcohols and diols under hydrogen gas, the presently most useful and efficient are complexes of transition metals, such as ruthenium, with bidentate phosphine-amine or tetradentate phosphine-imine ligands as described in Publication No. US 2010/0280273 A1 and in *Angew. Chem. Int. Ed.* **2007**, 46, 7473, incorporated herein by reference. Typical ruthenium catalyst loadings of 500 - 1000 ppm (0.05 – 0.1 mol%) are used, however, the major drawback of

such methods is the need for a large amounts of base (5-10 mol%) such as NaOMe, thereby reducing the product selectivity and generating large amounts of chemical waste due to the need for product neutralization and extensive purification. Furthermore, no hydrogenation of naturally occurring esters, e.g. plant oils such as olive oil, to give unsaturated fatty alcohols was reported with the ruthenium catalysts. Fatty alcohols behave as nonionic surfactants due to their amphiphilic nature. They find use as emulsifiers, emollients and thickeners in the cosmetics and food industries, and as industrial solvents. Fatty alcohols are also very useful in the production of detergents and surfactants, and they have a potential in the production of biodiesel.

[0004] The development of green chemical processes and the use of biomass for hydrogen production have attracted much attention in recent years. Significant progress in dehydrogenation of bio-alcohols (chiefly ethanol) has been achieved with heterogeneous catalysts, however, at the cost of using drastic reaction conditions, such as high temperature ($>200\text{ }^{\circ}\text{C}$) and pressure. Therefore, designing well-defined homogeneous catalysts for the dehydrogenation of alcohols under mild conditions represents an important scientific and practical goal.

[0005] There has been little progress in the area of acceptorless dehydrogenation of primary alcohols since Cole-Hamilton and co-workers demonstrated dehydrogenation of ethanol catalyzed by $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$, where an excess of NaOH, high temperature ($150\text{ }^{\circ}\text{C}$), and an intense light source were needed to achieve $\text{TOF} = 210\text{ h}^{-1}$, after 2 h (D. Morton, D. J. Cole-Hamilton, I. D. Utuk, M. Paneque-Sosa, M. Lopez-Poveda, *J. Chem. Soc. Dalton Trans.* 1989, 489; D. Morton, D. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* 1988, 1154; and D. Morton, D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* 1987, 248). In recent years, several new homogeneous catalysts for acceptorless dehydrogenative coupling of primary alcohols have been developed and studied, such as the systems published by Milstein and co-workers (for a review see: D. Milstein, *Top. Catal.* 2010, 53, 915). However, all these new catalysts are inactive at temperatures below $100\text{ }^{\circ}\text{C}$, for example, for converting ethanol and propanol to hydrogen and ethyl acetate and propyl propionate, respectively.

[0006] Therefore, there remains a need for efficient metal catalysts for the hydrogenation of esters, lactones, and fats and oils derived from natural sources, which could operate under base-free conditions and using relatively low reaction temperature and hydrogen pressure. There also

remains a need for catalysts capable of efficient alcohol dehydrogenation under mild, and preferably neutral, reaction conditions, for environmentally benign production of esters and lactones from alcohols and diols, respectively, accompanied by formation of hydrogen gas.

[0007] The above information is provided for the purpose of making known information believed by the applicant to be of possible relevance to the present invention. No admission is necessarily intended, nor should be construed, that any of the preceding information constitutes prior art against the present invention.

BRIEF DESCRIPTION OF THE FIGURES

[0008] For a better understanding of the present invention, as well as other aspects and further features thereof, reference is made to the following description which is to be used in conjunction with the accompanying drawings, where:

[0009] Figure 1 is an ORTEP diagram for complex 1, thermal ellipsoids are at 50% probability (the hydrogen atoms are omitted for clarity); and

[0010] Figure 2 is an ORTEP diagram for complex 2, thermal ellipsoids are at 50% probability (the hydrogen atoms are omitted for clarity).

[0011] Figure 3 is an ORTEP diagram for complex 7, thermal ellipsoids are at 50% probability (the hydrogen atoms except for NH are omitted for clarity).

DESCRIPTION OF THE INVENTION

[0012] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

[0013] As used in the specification and claims, the singular forms “a”, “an” and “the” include plural references unless the context clearly dictates otherwise.

[0014] The term “comprising” as used herein will be understood to mean that the list following is non-exhaustive and may or may not include any other additional suitable items, for example one or more further feature(s), component(s) and/or ingredient(s) as appropriate.

[0015] As used herein, “heteroatom” refers to non-hydrogen and non-carbon atoms, such as, for example, O, S, and N.

[0016] As used herein, “alkyl” means a hydrocarbon moiety that consists solely of single-bonded carbon and hydrogen atoms, for example a methyl or ethyl group.

[0017] As used herein, “alkenyl” means a hydrocarbon moiety that is linear, branched or cyclic and comprises at least one carbon to carbon double bond. “Alkynyl” means a hydrocarbon moiety that is linear, branched or cyclic and comprises at least one carbon to carbon triple bond. “Aryl” means a moiety including a substituted or unsubstituted aromatic ring, including heteroaryl moieties and moieties with more than one conjugated aromatic ring; optionally it may also include one or more non-aromatic ring. “C₅ to C₈ Aryl” means a moiety including a substituted or unsubstituted aromatic ring having from 5 to 8 carbon atoms in one or more conjugated aromatic rings. Examples of aryl moieties include phenyl.

[0018] “Heteroaryl” means a moiety including a substituted or unsubstituted aromatic ring having from 4 to 8 carbon atoms and at least one heteroatom in one or more conjugated aromatic rings. As used herein, “heteroatom” refers to non-carbon and non-hydrogen atoms, such as, for example, O, S, and N. Examples of heteroaryl moieties include pyridyl, furanyl and thienyl.

[0019] “Alkylene” means a divalent alkyl radical, e.g., $-\text{C}_f\text{H}_{2f}-$ wherein f is an integer.

“Alkenylene” means a divalent alkenyl radical, e.g., $-\text{CHCH}-$.

[0020]] “Substituted” means having one or more substituent moieties whose presence does not interfere with the desired reaction. Examples of substituents include alkyl, alkenyl, alkynyl, aryl, aryl-halide, heteroaryl, cycloalkyl (non-aromatic ring), Si(alkyl)₃, Si(alkoxy)₃, halo, alkoxyl, amino, alkylamino, alkenylamino, amide, amidine, hydroxyl, thioether, alkylcarbonyl, alkylcarbonyloxy, arylcarbonyloxy, alkoxycarbonyloxy, aryloxycarbonyloxy, carbonate, alkoxycarbonyl, aminocarbonyl, alkylthiocarbonyl, phosphate, phosphate ester, phosphonato, phosphinato, cyano, acylamino, imino, sulfhydryl, alkylthio, arylthio, thiocarboxylate,

dithiocarboxylate, sulfate, sulfato, sulfonate, sulfamoyl, sulfonamide, nitro, nitrile, azido, heterocyclyl, ether, ester, silicon-containing moieties, thioester, or a combination thereof. The substituents may themselves be substituted. For instance, an amino substituent may itself be mono or independently disubstituted by further substituents defined above, such as alkyl, alkenyl, alkynyl, aryl, aryl-halide and heteroaryl cycloalkyl (non-aromatic ring).

[0021] As used herein, the term " μ^Y " is used to indicate that a ligand is functioning as a bridging ligand, where a single atom bridges two metal atoms. The superscript "Y" denotes the atom bridging the two metal atoms. For example, the term " μ^N " is used to indicate that a ligand (or ligands) in a complex includes a nitrogen atom that bridges two metal atoms.

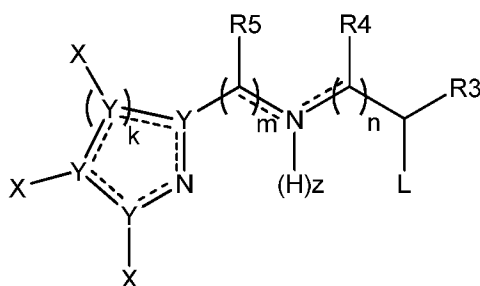
[0022] The present application provides a catalyst that is useful in a process of catalytic hydrogenation (reduction). The process is useful in hydrogenation of, for example, C_3-C_n ($n=4-200$) substrates possessing one or more ester or lactone groups to afford the corresponding alcohol, diol, or triol products. Thus, the present application further provides a practical reduction method that can be used in place of the main-group hydride reduction to obtain alcohols, diols, or triols in a simple, efficient, and "green" fashion, preferably using base-free reaction conditions. The catalyst of the present application is also useful in a process of catalytic dehydrogenation, which can be a homogeneous dehydrogenation process.

[0023] Catalyst

[0024] The processes described herein are carried out in the presence of a transition metal complex having a tridentate ligand LNN' .

[0025] In accordance with one aspect, there is provided a tridentate ligand LNN' comprising, in sequence, one phosphorus, sulfur, nitrogen or carbon group L, one amino or imino group N, and one heterocycle group N' .

[0001] In accordance with one embodiment, there is provided a compound of Formula I



I

wherein

L is a phosphine (PR^1R^2), a sulfide (SR^1), or a carbene group (CR^1R^2);

each Y is independently a C, N or S atom, wherein at least two Y's are C;

the dotted lines simultaneously or independently represent single or double bonds;

R^1 and R^2 are each independently H, or a C_1 - C_{20} linear alkyl, a C_3 - C_{20} branched alkyl, a C_3 - C_8 cycloalkyl, a C_2 - C_8 alkenyl, a C_5 - C_{20} aryl, each of which may be optionally substituted; or when taken together, R^1 and R^2 can together with L to which they are bound form a saturated or partially saturated ring;

R^3 and R^4 are each independently H, or a C_1 - C_8 linear alkyl, a C_3 - C_8 branched alkyl, a C_3 - C_8 cyclic alkyl, a C_2 - C_8 alkenyl, a C_5 - C_8 aryl, each of which may be optionally substituted; or R^3 and R^4 can join together to form a saturated heterocycle;

R^5 is H, a linear C_1 - C_8 alkyl, a branched C_3 - C_8 alkyl, a cyclic C_3 - C_8 alkyl, a C_2 - C_8 alkenyl, or a C_5 - C_8 aryl, each of which can be optionally substituted; or R^5 and R^4 can join together to form a saturated heterocycle;

each X is independently H, a linear C_1 - C_8 alkyl, a branched C_3 - C_8 alkyl, a cyclic C_3 - C_8 alkyl, a C_2 - C_8 alkenyl, or a C_5 - C_8 aryl, each of which can be optionally substituted, or OR, F, Cl, Br, I or NR_2 ; or when taken together, two of the X groups can together form an optionally substituted, saturated, partially saturated, aromatic or heteroaromatic ring;

R is H, a C_1 - C_{20} linear alkyl, a C_3 - C_{20} branched alkyl, a C_3 - C_8 cycloalkyl, a C_2 - C_8 alkenyl, or a C_5 - C_8 aryl, each of which may be optionally substituted;

each n and m is independently 1 or 2;

k is 1 or 2;

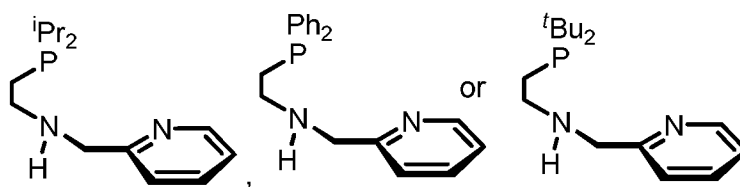
and

z is 0 or 1.

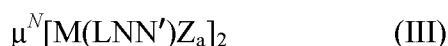
[0002] In accordance with one embodiment, R^3 and R^4 are each independently H, or C_1 - C_8 linear alkyl, C_3 - C_8 branched alkyl, cyclic alkyl C_3 - C_8 , C_1 - C_8 alkenyl, C_5 - C_8 aryl, each of which may be optionally substituted, or OR or NR_2 ; and R^5 is H, a linear C_1 - C_8 alkyl, branched C_3 - C_8 alkyl, cyclic C_3 - C_8 alkyl, C_3 - C_8 alkenyl, or C_5 - C_8 aryl, each of which can be optionally substituted, or OR or NR_2 . In one preferred embodiment, R^4 and R^5 are both H.

[0026] In accordance with another embodiment, each Y is C. In accordance with another embodiment, k is 2, and each X is H. In accordance with one preferred embodiment, L is a phosphene.

[0027] In accordance with one embodiment, the compound of Formula I is



[0028] In accordance with another aspect, there is provided a complex of Formula II or III



wherein:

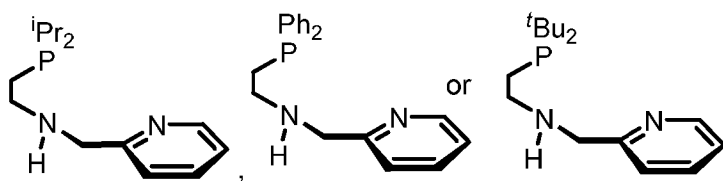
each Z is independently a hydrogen or halogen atom, a C_1 - C_6 alkyl, a hydroxyl, or a C_1 - C_6 alkoxy, a nitrosyl (NO) group, CO, CNR, or PR_3 , wherein R is an alkyl or an aryl, PMe_3 or PPh_3 ;

M is a transition metal; and

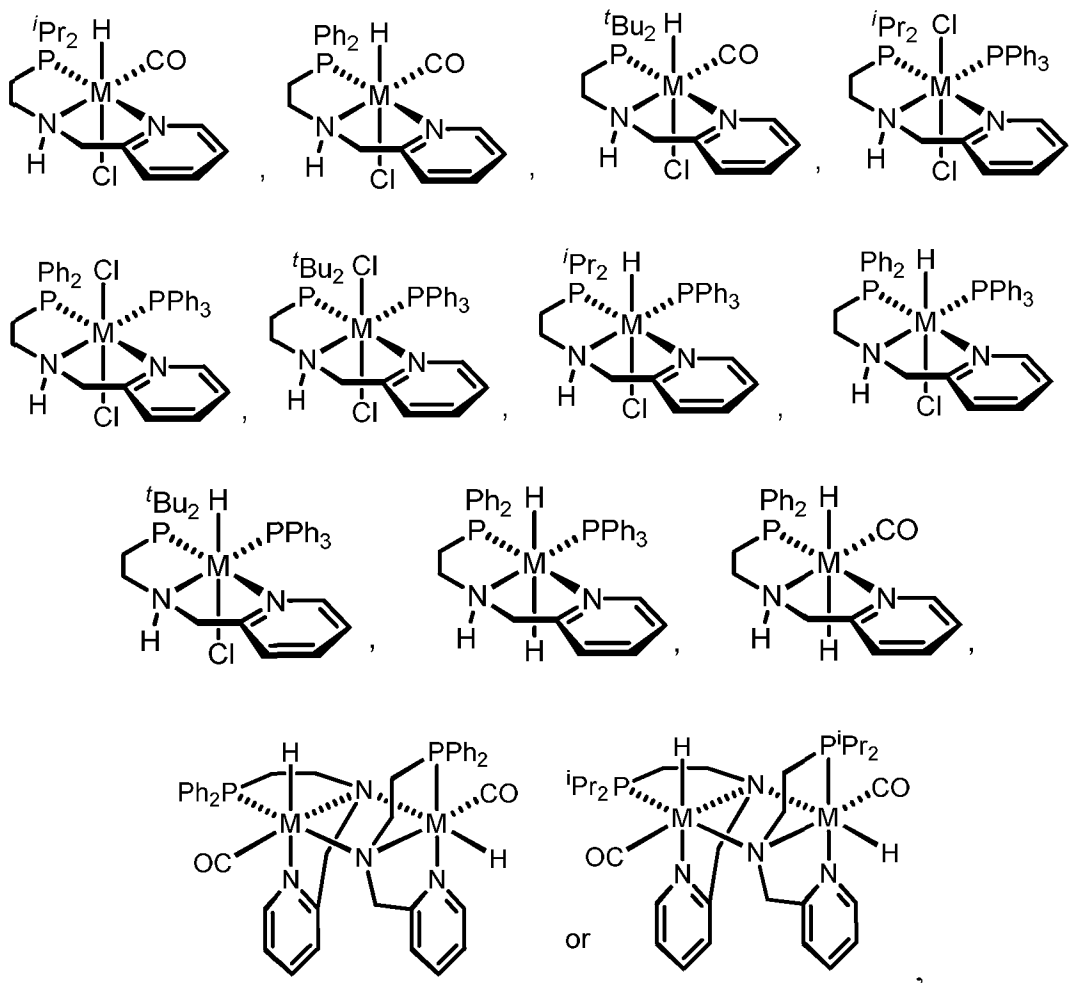
each LNN' is a coordinated ligand that is a compound of any one of claims 1-7.

[0029] In accordance with one embodiment, M is a group 7 metal, a group 8 metal or a group 9 metal. In accordance with one preferred embodiment, M is Ru or Os.

[0030] In accordance with another embodiment, the complex comprises the ligand LNN' , wherein LNN' is

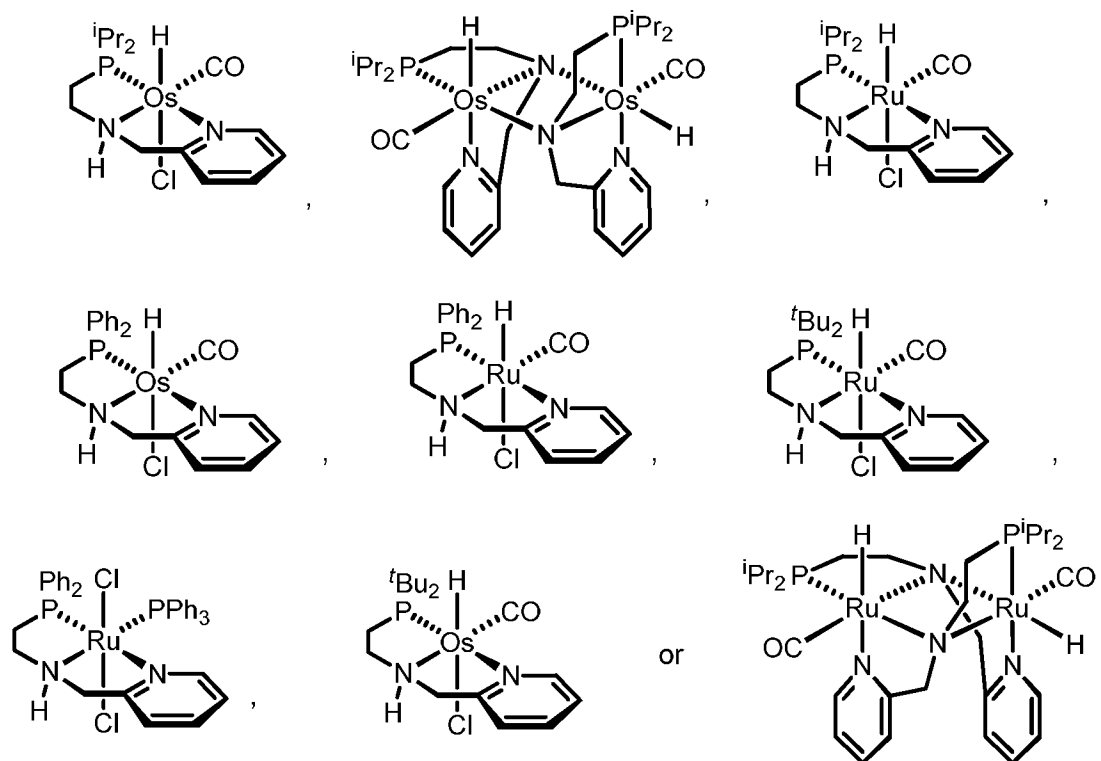


[0031] In accordance with another embodiment, the complex has the structure of

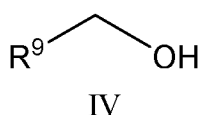


wherein M is as defined above.

[0032] In one preferred embodiment, the complex has the structure of any one of



[0033] In accordance with another aspect, there is provided a process for dehydrogenation of a substrate comprising treating the substrate with a catalytic amount of a complex as described. In one embodiment, the substrate is a compound of Formula IV



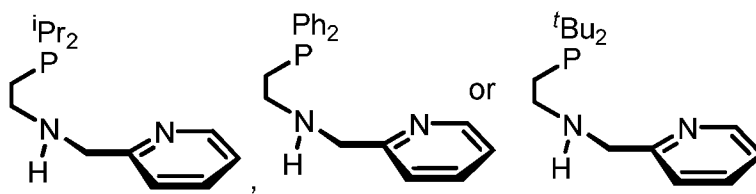
wherein R^9 is a C_{1-20} linear alkyl, a C_{3-20} branched alkyl, a C_{3-20} cycloalkyl, or an aryl, any of which may be optionally substituted.

[0034] In accordance with another aspect, there is provided a tridentate ligand LNN' having formula I, R^4 is H, a substituted or unsubstituted linear, branched or cyclic C_3 - C_8 alkyl or alkenyl, a substituted or an unsubstituted C_5 - C_8 aromatic group, and R^5 is a substituted or unsubstituted linear, branched or cyclic C_3 - C_8 alkyl or alkenyl, a substituted or unsubstituted C_5 - C_8 aryl.

[0035] In one embodiment, the heterocycle group N' of Formula I, wherein k is 1 or 2, the nitrogen heterocycle N' is optionally substituted and contains carbon, nitrogen, oxygen, or sulfur atoms Y. One preferred example of the heterocycle N' is the C₂-pyridyl group, C₅H₄N.

[0036] In another particular embodiment, L is an N-heterocyclic carbene. In another particular embodiment, L is a phosphene.

[0037] Some specific examples of tridentate ligands LNN' are:



[0038] The tridentate ligand LNN' described above can be synthesized using standard procedures. For example, the ligand can be obtained by condensation of optionally substituted 2-picolyl aldehyde (2-CHO-Py) with an aminophosphine or an optionally substituted thioamine. Reduction of the imine product by NaBH₄, Al(*t*Bu)₂H or any other reducing reagents well known in the state of the art will lead to the LNN' ligand of Formula I.

[0039] The presently described tridentate ligands are of relatively low cost to produce. The reduced cost is at least partially the result of the use of less expensive chemicals as well as surprisingly high efficiency of ligand synthesis. Production of the present ligands are already order of magnitude less expensive than other examples of tridentate ligands used in catalyst complexes in the literature.

[0040] According to another aspect, there are provided complexes of the general Formulae II and III:



wherein LNN' is the tridentate ligand of Formula I and a equals 2 or 3. Each Z represents simultaneously or independently a hydrogen or halogen atom, a C₁-C₆ alkyl radical, a hydroxyl

group, or a C₁-C₆ alkoxy radical, a nitrosyl (NO) group, CO, CNR (R=Alkyl, Aryl), PMe₃ or PPh₃, and M is a transition metal. The complexes as presently described may exist in both neutral and cationic forms.

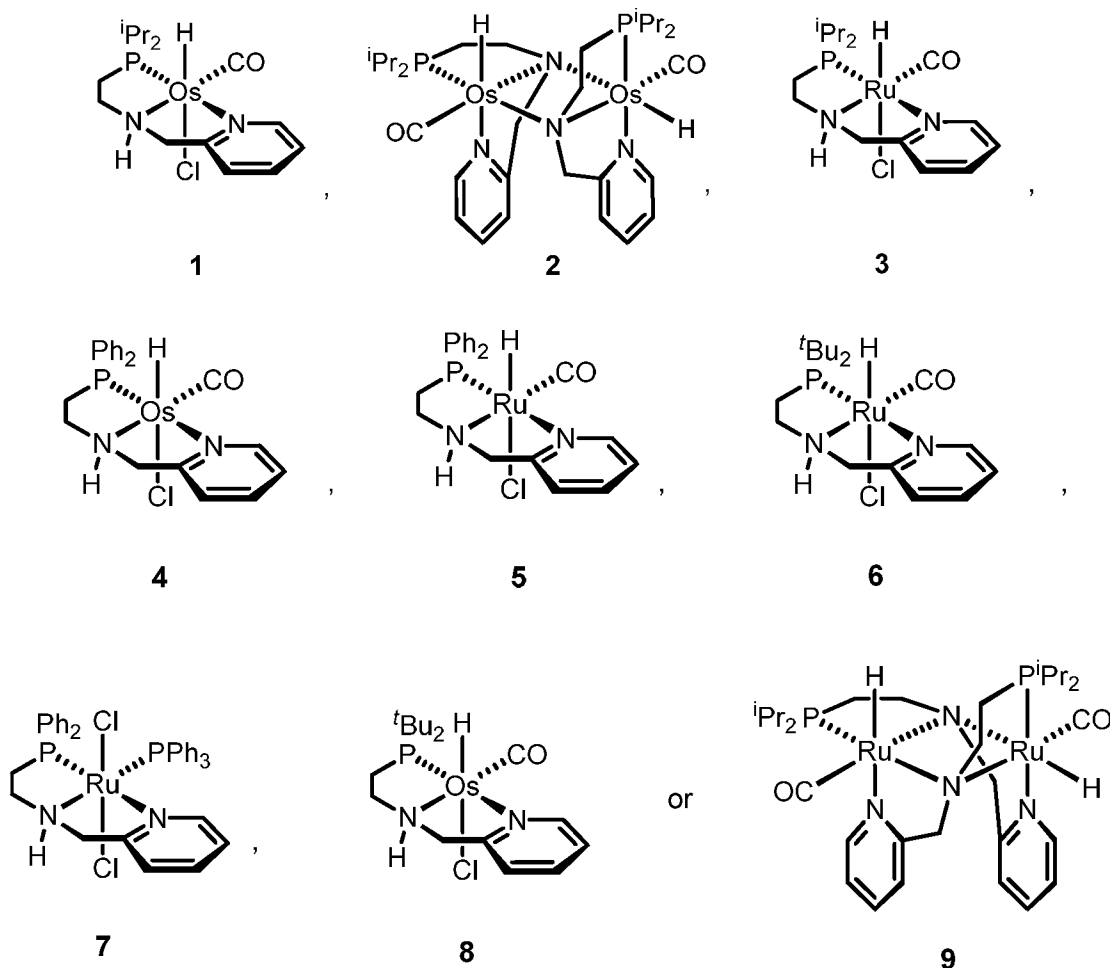
[0041] In accordance with one embodiment, the transition metal M is preferably a metal from groups 7 (manganese group), 8 (iron group), and 9 (cobalt group). In one preferred embodiment, the transition metal is Ru or Os.

[0042] In one embodiment, the complex of Formula II can be prepared by reaction of the LNN' ligand of Formula I with a metal precursor, such as those well known in the state of the art. Preferably, the metal precursor is a ruthenium or osmium compound, including, for example, the following formulae: RuHCl(CO)(AsPh₃)₃, RuCl₂(CO)(AsPh₃)₃, RuHCl(CO)(PPh₃)₃, RuCl₂(CO)(PPh₃)₃, OsHCl(CO)(AsPh₃)₃, OsCl₂(CO)(AsPh₃)₃, OsHCl(CO)(PPh₃)₃, OsCl₂(CO)(PPh₃)₃, [RuCl₂(p-cymene)]₂, [OsCl₂(p-cymene)]₂, RuCl₂(CO)(p-cymene), OsCl₂(CO)(p-cymene), RuCl₂(CO)(DMF)(PPh₃)₂, [IrCl(COD)]₂, [IrCl(COE)]₂, IrHCl₂(PPh₃)₃, IrH₂Cl(PPh₃)₃, IrHCl₂(AsPh₃)₃, or IrH₂Cl(AsPh₃)₃. The reactions can be conducted in various organic solvents, such as, but not limited to, toluene, xylene, benzene, diglyme, DMF or DME.

[0043] In accordance with another embodiment, transformation of a complexes of Formula II to a complex of Formula III can be achieved using a base. Non-limiting examples of suitable bases include group I salts (such as Li, Na, K) of alkoxides, such as t-butoxide, and amides, such as N(TMS)₂. One specific examples of an acceptable base is potassium t-butoxide. In certain, non-limiting, examples, the base has a pK_a > 11. Additional non-limiting examples of suitable bases are group I salts or ammonium of hydroxides, alcoholates, alkaline carbonates, amides, siliconates, hydrides, borohydrides, aluminum hydrides, where the group I salt is Li, Na, K, or ammonium salts of the formula NR₄, and R is alkyl, aryl or H.

[0044] Complexes of Formulae II and III can be prepared prior to hydrogenation or *in situ* using above bases. Preparation of complexes of Formula II and III can be performed in various solvents, such as, but not limited to THF, Et₂O, toluene, benzene, diglyme, DMF or DME or any other appropriate solvents known to the person skilled in the art.

Structures of exemplary complexes **1-9** are shown below:

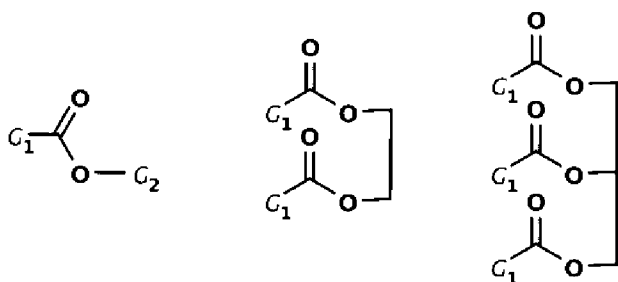


[0045] In another aspect, there is provided a process for making ethyl acetate comprising treating ethanol with a catalytic amount of a complex as described herein. In one embodiment, the process of is a homogeneous process. In another embodiment, the process does not require a hydrogen acceptor.

[0046] Hydrogenation Process

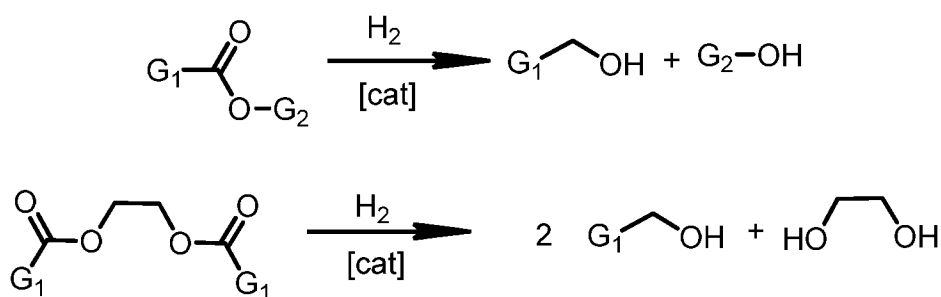
[0047] The present application additionally provides a catalytic hydrogenation process. The catalyst complexes of Formulae II and III described above, have been found to show high selectivity toward reduction of the ester groups in the presence of C=C double bonds. This provides a useful way of deriving unsaturated alcohols from natural products such as, but not limited to, olive or canola oils, under mild reduction conditions.

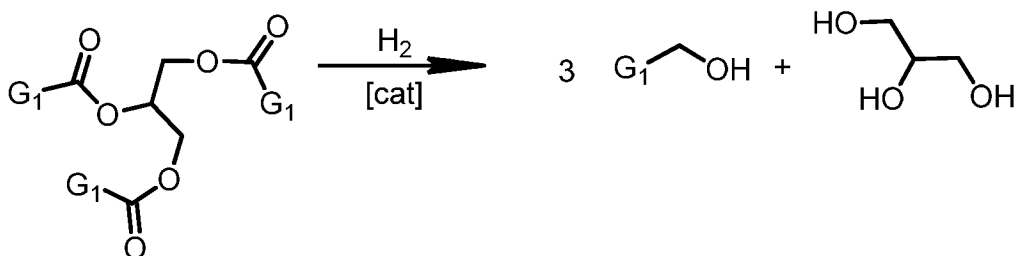
[0048] In one embodiment, there is provided a process for hydrogenation of esters using metal catalysts based on the LNN' ligand of Formula I. According to specific embodiment, the substrates are compounds of the following formulae:



[0049] The term “substrate”, as used herein and as commonly understood, refers to the reactant that will be converted to a product during a catalytic reaction. Groups G_1 and G_2 , simultaneously or independently, represent a linear, branched C_1 - C_{40} or cyclic C_3 - C_{40} alkyl, alkenyl or aromatic group, optionally substituted. Also, one may cite a situation when G_1 and G_2 together form a C_4 - C_{40} saturated or an unsaturated radical. The substrate of the hydrogenation reaction can be any organic compound containing one, or more than one, carboalkoxy group. In this respect, natural fats such as olive, canola, corn, peanut, palm and other plant oils are useful substrates that can be reduced to form a mixture of alcohols.

[0050] The reduction or hydrogenation reaction proceeds, generally, according to the one of the reactions scheme below:





wherein G_1 and G_2 are independently selected from any optionally substituted hydrocarbon group. For clarity, where multiple substituents G_1 occur in the same molecule, it is understood that each of these substituents can be a different optionally substituted hydrocarbon.

[0051] When the substrate is a monoester or a lactone, the products are alcohols or a diol, respectively. The naturally occurring triglycerides, oils and fats, can be reduced to glycerol and the corresponding fatty alcohols.

[0052] According to one embodiment of the invention, the process of catalytic reduction of esters implies the usage of at least one of the metal complexes **1** or **2**, hydrogen pressure, and optionally a base and a solvent. The base may be necessary in those cases when the metal catalyst **1** contains one or more halogen atoms bonded to the metal. The treatment with base can be done prior to the reduction or *in situ* by adding base to the reaction mixture during hydrogenation. The catalysts and pre-catalysts of this invention can be used in a wide range of concentration, preferably between 10-1000 ppm, and the loadings of 500 ppm or less are particularly preferred. The preferred amount of the catalyst will depend, as it is known to the person skilled in the art, on the type of the substrate, and increasing the catalyst loading should result in faster hydrogenation. The temperature at which the hydrogenation can be carried out is comprised between 0 °C and 150 °C, more preferably in the range between 50 °C and 100 °C and, as it is known to the person skilled in the art, the reaction rate will increase with increase of the reaction temperature. The hydrogenation reaction needs a pressure of H_2 gas and should be performed in a suitable pressure vessel. The surface area of the reactor as well as the hydrogen pressure, as it is known to the person skilled in the art, can greatly influence the reaction rate. The greater are the hydrogen pressure and the surface area of the reactor, the faster is the hydrogenation reaction rate. One may cite the hydrogen pressure in range of 10-200 Bar. Again, the person skilled in the art is well able to adjust the pressure as a function of the catalyst load

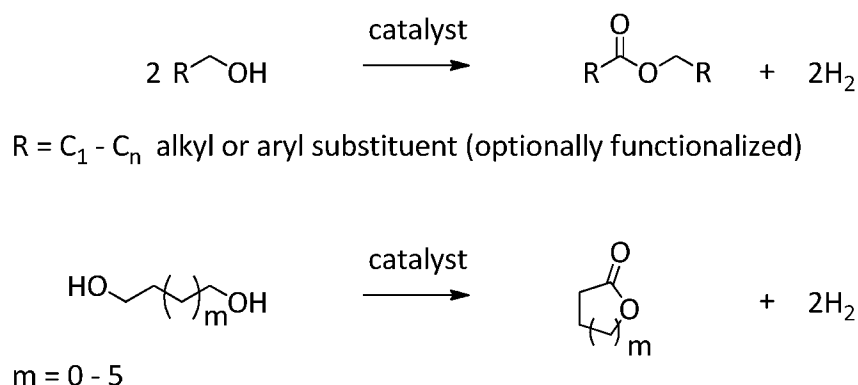
and of the dilution of the substrate in the solvent. As examples, one can cite typical pressures of 5 to 50 bar (5 to 50×10^5 Pa).

[0053] It should be well understood, however, that the catalyst complexes described herein are also useful in catalyzing hydrogenation of substrates including functional groups other than esters. The table below provides a non-limiting list of substrates and corresponding products that can be formed from a catalytic hydrogenation reaction using a catalyst of Formula II or III.

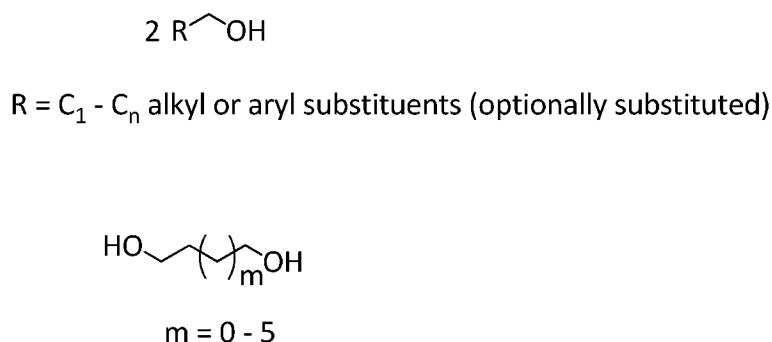
Hydrogenation Substrate	Product
aldehyde	alcohol
ketone	alcohol
ester	alcohol
carboxylic acid	alcohol
ketene	alcohol
enol	alcohol
epoxide	alcohol
aldimine	amine
ketimine	amine
ketene-imine	amine
nitrile	amine
aziridine	amine
nitro	amine
diazo	amine
isocyanide	amine
enamine	amine
lactone	diol
amide	amine + alcohol
aminoboranes	amine-borane
borazine	amine-borane
olefin	alkane
acetylene	alkane
allene	alkane

[0054] Dehydrogenation Reaction

[0055] The present application further provides a process of catalytic dehydrogenation using the catalyst complexes of Formulae II and III. For example, this catalyst or precatalyst is suitable for dehydrogenation of C₂-C_n (n=4-200) alcohols possessing one or more –CH₂OH groups thereby affording hydrogen gas and the corresponding esters or lactons, according to the following scheme. In one embodiment this process is a homogeneous dehydrogenation process, that can be used in place of the existing heterogeneous techniques, preferably using base-free reaction conditions and avoiding high reaction temperatures.



[0056] Accordingly, one embodiment provides a process for dehydrogenation of alcohols using metal catalysts based on the LNN' ligand of Formula I. According to an embodiment of the invention, the substrates are compounds of the following formulae:



[0057] In this embodiment, R groups, simultaneously or independently, represent a linear, branched C₁-C₄₀ or cyclic C₃-C₄₀ alkyl, alkenyl or aromatic group, optionally substituted. Also, one may cite a situation when R is C₄-C₄₀ saturated or an unsaturated cyclic radical. This implies that the substrate can be any organic compound containing one, or more than one, hydroxyl

(-OH) group. When the substrate is an alcohol or diol, the products are an ester or a lactone, respectively.

[0058] According to one embodiment, the process of catalytic acceptorless dehydrogenation implies the usage of at least one of the metal complexes of Formulae II or III and (optionally) the use of a base and a solvent. The base may be necessary in those cases when the metal catalyst of Formula II contains one or more halogen or alkoxy (-OR) groups bonded to the metal. The catalyst can be treated with base prior to mixing with the substrate or *in situ* by adding base to the reaction mixture during dehydrogenation. The catalysts and pre-catalysts described herein can be used in a wide range of concentration, preferably between 10-1000 ppm, and the loadings of 1000 ppm or less are particularly preferred. The preferred amount of the catalyst will depend, as it is known to the person skilled in the art, on the type of the substrate; and increasing the catalyst loading should result in faster dehydrogenation. The temperature at which the dehydrogenation can be carried out is comprised between 0 °C and 200 °C, more preferably in the range between 50 °C and 150 °C and, as it is known to the person skilled in the art, the reaction rate will increase with increase of the reaction temperature. The dehydrogenation process can generate a pressure of H₂ gas and, in such case, can be performed in a suitable pressure vessel, if necessary equipped with a pressure-release valve.

[0059] It should be well understood, however, that the catalyst complexes described herein are also useful in catalyzing dehydrogenation of substrates including functional groups other than alcohols. The table below provides a non-limiting list of substrates and corresponding products that can be formed from a catalytic dehydrogenation reaction using a catalyst of Formula II or III.

Substrate	Product ^a
alcohols	ester
alcohol	aldehyde
alcohol	ketone
diol	lactone
amine + alcohol	amide
amine + alcohol	substituted amine
amine + alcohol	imine

Substrate	Product ^a
ammonia-borane	aminoboranes
ammonia-borane	borazine
amine	imine
amines	guanidine
alcohol + thiol	thioester
thiol	sulphoxide
alcohol + phosphine	acyl phosphine

^a H₂ is also a byproduct of these reactions. It is either liberated from the reaction as H₂ or transferred to an acceptor.

[0060] As noted above, a byproduct of the dehydrogenation reactions is H₂. Accordingly, the present application further provides a process for producing H₂. The process can conveniently make use of readily available substrates in a straightforward catalytic dehydrogenation process under relatively mild conditions to generate H₂.

[0061] To gain a better understanding of the invention described herein, the following examples are set forth. It should be understood that these examples are for illustrative purposes only. Therefore, they should not limit the scope of this invention in any way.

EXAMPLES

[0062] Unless mentioned otherwise, all manipulations were performed under an inert gas (argon or nitrogen) in gloveboxes or using standard Schlenk techniques. NMR spectra were recorded on a Varian Unity Inova 300 MHz spectrometer. All ³¹P chemical shifts are relative to 85% H₃PO₄. ¹H and ¹³C chemical shifts were measured relative to the solvent peaks but are reported relative to TMS. OsO₄ and RuCl₃·3H₂O were purchased from Pressure Chemicals. All other chemicals and anhydrous grade solvents were obtained from Aldrich and Alfa Aesar. Commercial anhydrous grade ethanol was further distilled over sodium metal and stored in the argon glovebox. (NEt₄)₂OsCl₆, RuHCl(CO)(AsPh₃)₃, OsHCl(CO)(AsPh₃)₃, RuCl₂(PPh₃)₃, RuCl₂(CO)(DMF)(PPh₃)₂ were prepared according to previously reported methods. (Gusev, D. G., Dolgushin, F. M., Antipin, M. Yu. *Organometallics* 2001, 20, 1001; Spasyuk, D., Smith, S., Gusev, D. G. *Angew. Chem.* 2012, 51, 2772–2775; Shaw, A. P., Ryland, B. L., Norton, J. R., Buccella, D., Moscatelli, A. *Inorg. Chem.* 2007, 46, 5805–5812; Rajagopal, S., Vancheesan, S.,

Rajaram, J., Kuriacose, J. C. J. Mol. Cat. 1983, 22, 131–135, all incorporated herein by reference.)

[0063] Example 1 - Synthesis of $\text{PyCH}_2\text{NH}(\text{CH}_2)_2\text{N}(\text{iPr})_2$

[0064] 2-aminoethyl diisopropylamine (6.32 g, 0.044 mmol) was added to 2-picolyl aldehyde (4.70 g, 0.044 mmol) and the mixture was stirred for 1 h. The obtained imine was diluted with methanol (15 mL) and NaBH_4 (1.66 g, 0.044 mmol) was added portion-wise during 1h. Then, all volatiles were removed under vacuum, and the residue was re-dissolved in 20 mL of dichloromethane. The solution was filtered through a short pad (3×2 cm) of Al_2O_3 . The aluminum oxide was then washed with 10 mL of dichloromethane and the collected filtrate was evaporated and dried under vacuum for 1 h. The product was obtained as a yellow oil (8.41 g, 90 %).

[0065] ^1H NMR (300 MHz, CDCl_3) δ = 8.47 (ddd, J =4.8, 1.8, 0.9 Hz, 1H), 7.73 (td, J =7.6, 1.8 Hz, 1H), 7.39 (d, J =7.8 Hz, 1H), 7.21 (ddd, J =7.5, 4.9, 1.2 Hz, 1H), 3.77 (s, 2H), 3.33 (br., 1H, NH), 2.97 (sep, J =7.0, 2H; CH), 2.48 (m, J =2.5 Hz, 4H, CH_2), 0.92 (d, J =6.6 Hz, 12H; $4 \times \text{CH}_3$). ^{13}C NMR ($[\text{D}_6]\text{DMSO}$) δ = 160.62 (s, 1C; Py), 148.75 (s, 1C; Py), 136.33 (s, 1C; Py), 121.75 (s, 1C; Py), 121.65 (s, 1C; Py), 54.71 (s, 1C; CH_2), 49.23 (s, 1C; CH_2), 47.65 (s, 2C; CH), 44.14 (s, 1C; CH_2), 20.72 (s, 1C; $4 \times \text{CH}_3$).

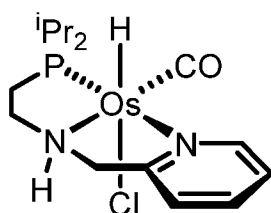
[0066] Example 2 - Synthesis of $\text{PyCH}_2\text{NH}(\text{CH}_2)_2\text{P}(\text{iPr})_2$

[0067] 2-picolyl aldehyde (1.66 g, 0.0155 mmol) in 10 mL of THF was added to a 10 wt% solution of 2-(di-*i*-propylphosphino)ethylamine in THF (26.0 g, 0.0162 mmol) and the mixture was stirred for 1 h. The obtained imine was then treated with diisobutyl aluminum hydride (22.7 mL, 1.5 M in toluene, 0.0341 mmol) during 1h (Caution!!! Exothermic reaction!) and left to stir for 1 h. After that time, the solution was quenched with 1 mL of water (Caution!!! Exothermic reaction!) and the obtained suspension was filtered through a short pad (3×2 cm) of basic alumina. The solids were washed with THF (3 ? 10 mL) and the collected filtrate was evaporated and dried under vacuum for 3 h. The product was obtained as a yellow oil (2.84 g, 73 %).

[0068] $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_6]\text{Benzene}$) δ = -1.0 (s). ^1H NMR ($[\text{D}_6]\text{Benzene}$) δ = 8.49 (dt, J =4.7, 1.8 Hz, 1H; Py), 7.15 – 7.13 (m, 1H; Py), 7.09 (td, J =7.7, J =1.8 Hz, 1H; Py), 6.64 (ddd, J =7.0,

4.9, 1.7 Hz, 1H; Py), 3.93 (s, 2H; PyCH₂), 2.81 (m, 2H; NCH₂), 1.78 (br. s, 1H; NH), 1.65 – 1.35 (m, 4H; PCH and CH₂P), 1.01 (dd, $J=13.8$, 7.1 Hz, 6H; CH₃), 0.96 (dd, $J=10.8$, 7.0 Hz, 6H; CH₃). ¹³C{¹H} NMR ([D₆]Benzene) δ = 161.37 (s, 1C; Py), 149.49 (s, 1C; Py), 135.85 (s, 1C; Py), 121.92 (s, 1C; Py), 121.60 (s, 1C; Py), 55.72 (s; 1C; NCH₂), 49.12 (d, $J(\text{CP})=24.9$ Hz, 1C; NCH₂), 23.72 (d, $J(\text{CP})=13.5$ Hz, 2C; PCH), 23.37 (d, $J(\text{CP})=19.3$ Hz, 1C; PCH₂), 20.29 (d, $J(\text{CP})=16.5$ Hz, 2C; CH₃), 18.93 (d, $J(\text{CP})=9.9$ Hz, 2C; CH₃).

[0069] Example 3 - Synthesis of *trans*-OsHCl(CO)[PyCH₂NH(CH₂)₂P(*i*Pr)₂]



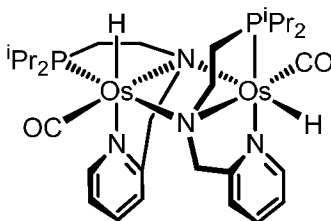
Complex 1

[0070] A flask containing a mixture of OsHCl(CO)(AsPh₃)₃ (5.94 g, 5.57 mmol) and PyCH₂NH(CH₂)₂P(*i*Pr)₂ (1.27 g, 5.06 mmol) in 15 mL of diglyme was placed in a preheated to 160 °C oil bath and stirred for 1 h, affording a dark-red solution. After cooling to room temperature, the mixture was diluted with 4 mL of diethylether, and the flask was stored overnight in a freezer at 18 °C. The precipitated product was filtered off, washed with diethyl ether (3 × 3 mL), and dried under vacuum for 3 h to give a brown crystalline solid. Yield: 1.81 g (71%).

[0071] ³¹P{¹H} NMR ([D₂]DCM) δ = 48.41 (s). ¹H{³¹P} NMR ([D₂]DCM) δ = 9.00 (d, $J=5.5$ Hz, 1H, Py), 7.68 (td, $J=7.8$, 1.5 Hz, 1H, Py), 7.28 – 7.16 (m, 1H, Py), 4.61 (dd, $J=14.3$, 4.4 Hz, 1H, PyCH₂), 4.12 (br. t, $J=12.0$ Hz, 1H, NH), 3.93 (dd, $J=14.2$, 11.6 Hz, 1H, PyCH₂), 3.67 – 3.58 (m, 1H, NCH₂), 2.73 – 2.53 (m, 1H, NCH₂), 2.46 (sep, $J=14.7$, 7.4 Hz, 1H, PCH), 2.37 (dd, $J=15.0$, 4.0 Hz, 1H, CH₂P), 2.11 (sept, $J=6.9$ Hz, 1H, PCH), 1.77 (td, $J=14.6$, 5.8 Hz, 1H, CH₂P), 1.35 (d, $J=7.4$ Hz, 3H, CH₃), 1.21 (d, $J=7.2$ Hz, 3H, CH₃), 1.09 (d, $J=6.9$ Hz, 3H, CH₃), 1.04 (d, $J=7.0$ Hz, 3H, CH₃), -16.45 (s, 1H, OsH, satellites $J(\text{OsH})=95.22$). ¹³C{¹H} NMR ([D₂]DCM) δ = 188.57 (d, $J(\text{CP})=8.6$ Hz, CO), 161.56 (s, 1C, Py), 153.89 (d, $J(\text{CP})=1.7$ Hz, 1C; Py), 136.16 (s, 1C; Py), 125.13 (d, $J(\text{CP})=2.0$ Hz, 1C; Py), 121.80 (d, $J(\text{CP})=1.7$ Hz, 1C; Py), 60.62 (d,

$J(\text{CP})=2.3$ Hz, 1C; CH₂), 54.96 (d, $J(\text{CP})=1.7$ Hz, 1C; CH₂), 33.07 (d, $J(\text{CP})=25.9$ Hz, 1C; CH), 29.19 (d, $J(\text{CP})=30.3$ Hz, 1C; CH), 26.03 (d, $J(\text{CP})=33.1$ Hz, 1C; CH₂), 21.04 (d, $J(\text{CP})=3.9$ Hz, 1C; CH₃), 20.57 (d, $J(\text{CP})=3.4$ Hz, 1C; CH₃), 19.05 (s, 1C; CH₃), 17.51 (d, $J(\text{CP})=4.6$ Hz, 1C; CH₃). IR (Nujol): $\nu_{\text{C=O}}=1879$ (s) Anal. Calc'd for C₁₅H₂₆ClN₂OOSp: C, 35.53; H, 5.17; N, 5.24. Found: C, 35.35; H, 5.19; N, 5.24.

[0072] Example 4 - Synthesis of μ^{N} -mer, fac- $\{\text{OsH}(\text{CO})[\text{PyCH}_2\text{N}(\text{CH}_2)_2\text{P}(\text{iPr})_2]\}_2$



Complex 2

[0073] A mixture of OsHCl(CO)[PyCH₂NH(CH₂)₂P(*i*Pr)₂] (1.00 g, 1.97 mmol) and KO^{*t*}Bu (243 mg, 2.17 mmol) in 7 mL of THF was stirred for 2 h, then the resulting solution was placed in a freezer for 1 h. The red reaction mixture was filtered into a 20 mL vial, and 1 mL of THF was used to rinse the fritted funnel. The solution was diluted with 6 mL of diethyl ether and the compound was crystallized in a freezer at -18 °C. The crystalline bright-yellow product was isolated by filtration and dried under vacuum for 1 h. Yield: 621 mg (67%).

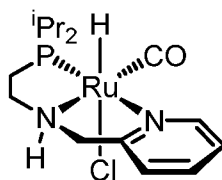
[0074] ³¹P NMR ([D₂]DCM) δ = 67.73 (s), 51.50 (s). ¹H{³¹P} NMR ([D₂]DCM) δ = 8.86 (t, $J=6.7$ Hz, 2H, Py), 7.08 (t, $J=7.8$ Hz, 1H, Py), 7.01 (t, $J=7.6$ Hz, 1H, Py), 6.86 – 6.73 (m, 2H, Py), 6.34 (d, $J=8.0$ Hz, 1H, Py), 6.24 (d, $J=7.8$ Hz, 1H, Py), 5.24 (d, $J=17.8$ Hz, 1H, PyCH₂), 4.72 (d, $J=19.4$ Hz, 1H, PyCH₂), 4.14 (d, $J=17.7$ Hz, 1H, NCH₂), 3.84 (t, $J=12.9$ Hz, 1H, NCH₂), 3.80 – 3.68 (m, 1H), 3.56 – 3.33 (m, 3H), 2.75 (hept, $J=14.4$, 1H; CH), 2.39 – 2.17 (m, 2H), 2.05 (hept, $J=5.6$, 1H, PCH), 1.99 – 1.87 (m, 1H), 1.83 – 1.62 (m, 1H), 1.32 (2d overlapped, $J=7.4$ Hz, 3H), 1.28 – 1.16 (m, 1H), 1.09 (d, $J=6.9$ Hz, 3H; CH₃), 1.05 (d, $J=6.8$ Hz, 3H; CH₃), 0.95 (d, $J=6.7$ Hz, 3H; CH₃), 0.89 (d, $J=6.9$ Hz, 3H; CH₃), 0.73 (d, $J=7.0$ Hz, 3H; CH₃), 0.58 (t, $J=7.3$ Hz, 3H), -11.54 (s, 1H; OsH), -14.31 (s, 1H; OsH). ¹³C{¹H} NMR ([D₂]DCM) δ = 191.26 (d, $J(\text{CP})=9.0$ Hz, 1C; CO), 190.06 (d, $J(\text{CP})=6.7$ Hz, 1C; CO), 171.19 (s, 1C; Py), 170.65 (s, 1C; Py), 151.05 (s, 1C; Py), 150.77 (s, 1C; Py), 133.61 (s, 1C; Py), 133.36 (s, 1C; Py), 122.96 (d,

$J(\text{CP})=2.0$ Hz, 1C; Py), 122.80 (s, 1C; Py), 117.82 (s, 1C; Py), 75.84 (s, 1C; PyCH₂), 74.06 (s, 1C; PyCH₂), 70.28 (d, $J(\text{CP})=6.5$ Hz, 1C; NCH₂), 68.89 (s, 1C; NCH₂), 36.42 (d, $J(\text{CP})=28.7$ Hz, 1C; CH), 30.73 (d, $J(\text{CP})=21.3$ Hz, 1C; CH), 29.15 (d, $J(\text{CP})=36.4$ Hz, 1C; CH), 28.59 (d, $J(\text{CP})=21.8$ Hz, 1C; CH), 26.46 (d, $J(\text{CP})=22.2$ Hz, 1C; CH₂), 26.01 (d, $J(\text{CP})=32.2$ Hz, 1C; CH₂), 22.32 (d, $J(\text{CP})=3.6$ Hz, 1C; CH₃), 20.91 (d, $J(\text{CP})=4.7$ Hz, 1C; CH₃), 20.17 (d, $J(\text{CP})=2.3$ Hz, 1C; CH₃), 19.77 (s, 1C; CH₃), 19.58 (d, $J(\text{CP})=2.3$ Hz, 1C; CH₃), 19.09 (s, 1C; CH₃), 18.26 (s, 1C; CH₃), 16.77 (d, $J(\text{CP})=7.0$ Hz, 1C; CH₃).

[0075] Example 5 - Synthesis of RuHCl(CO)(AsPh₃)₃

[0076] A 250 mL round-bottom Schlenk flask was loaded in air with RuCl₃·3H₂O (1.26 g, 4.85 mmol), AsPh₃ (5.94 g, 19.4 mmol), NEt(*i*Pr)₂ (5.00 g, 38.7 mmol), 2-methoxyethanol (115 mL) and aqueous formaldehyde (40%, 15 mL). The stoppered flask was briefly opened to vacuum and refilled with argon; this procedure was repeated five times. The stirred reaction mixture was heated in an oil bath for 4 h while maintaining the bath temperature at 125 °C. The resulting greyish suspension was left at room temperature for 1 h. The precipitate was filtered off, washed with ethanol (3 × 5 mL), and dried under vacuum for 2 h to give an off-white solid. Yield: 3.14 g (66%).

[0077] Example 6 - Synthesis of *trans*-RuHCl(CO)[PyCH₂NH(CH₂)₂P(*i*Pr)₂]



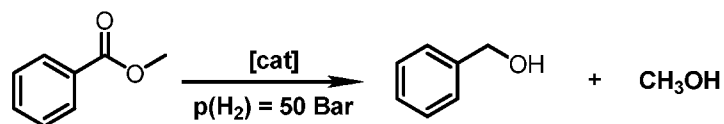
Complex 3

[0078] A 25 mL Schlenk flask containing a mixture of RuHCl(CO)(AsPh₃)₃ (2.13 g, 2.18 mmol) and PyCH₂NH(CH₂)₂P(*i*Pr)₂ (500 mg, 1.98 mmol) in 20 mL of toluene was stirred under reflux for 1 h at 110°C affording a dark brown solution. After cooling to room temperature, the product was filtered giving a pale brown powdery solid that was washed with diethylether (2 × 5 mL) and dried under vacuum. Yield: 671 mg (81%).

[0079] $^{31}\text{P}\{^1\text{H}\}$ NMR ([D₂]DCM) δ = 94.74 (s). $^1\text{H}\{^{31}\text{P}\}$ NMR ([D₂]DCM) δ = 8.93 (d, J =5.3 Hz, 1H; Py), 7.68 (td, J =7.7, 1.6 Hz, 1H; Py), 7.32 – 7.12 (m, 2H; Py), 4.41 (d, J =10.2 Hz, 1H; CH₂), 4.20 – 3.95 (m, 2H; NH + CH₂), 3.57 – 3.40 (m, 1H; CH₂), 2.62 (ddd, J =11.3, 9.3, 3.9 Hz, 1H; CH₂), 2.50 (sep, J =7.1 Hz, 1H; CH), 2.30 (dd, J =15.0, 3.8 Hz, 1H; CH₂), 2.19 (sep, J = 6.9 Hz, 1H; CH), 1.91 (td, J =14.6, 5.9 Hz, 1H; CH₂), 1.38 (d, J =7.4 Hz, 3H; CH₃), 1.21 (d, J =7.2 Hz, 3H; CH₃), 1.15 – 1.01 (overlapped d, 6H; 2CH₃), -14.93 (s, 1H; RuH). $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₂]DCM) δ = 206.52 (dd due to coupling to ^{31}P and the residual coupling to the hydride, $J(\text{CP})$ =15.3, 7.3 Hz, 1C; CO), 160.91 (s, 1C; Py), 153.65 (d, $J(\text{CP})$ =1.3 Hz, 1C; Py), 136.79 (s, 1C; Py), 124.42 (d, $J(\text{CP})$ =2.0 Hz, 1C; Py), 121.57 (d, $J(\text{CP})$ =1.5 Hz, 1C; Py), 59.80 (s, 1C; PyCH₂), 52.98 (s, 1C; NCH₂), 32.58 (d, $J(\text{CP})$ =21.3 Hz, 1C; PCH₂), 29.02 (d, $J(\text{CP})$ =24.9 Hz, 1C; CH), 25.03 (d, $J(\text{CP})$ =28.5 Hz, 2C; CH), 20.69 (d, $J(\text{CP})$ =4.2 Hz, 2C; 2×CH₃), 19.05 (s, 1C; CH₃), 17.61 (d, $J(\text{CP})$ =5.2 Hz, 1C; CH₃).

[0080] Example 7 - Hydrogenation of esters using complexes 1

[0081] *t*BuOK (15 mg, 0.13 mmol) was added to a solution of complex **1** (51 mg, 0.10 mmol) in 10 mL of THF and the mixture was stirred for 3 min. 1 mL of the obtained solution was mixed with methyl benzoate (2.72 g, 20.0 mol) or other desired substrate in 6 mL of THF or toluene. The mixture was then placed into a 75 mL stainless-steel reactor (Parr 4740) equipped with a magnetic stir bar. The reactor was purged by two cycles of pressurization/venting with H₂ (150 psi, 10 Bar) and then pressurized with H₂ (725 psi, 50 Bar) and disconnected from the H₂ source. The reaction was conducted for 1.5 h at 100 °C in a preheated oil bath. At the end of the reaction time, the reactor was placed into a cold water bath and it was depressurized after cooling to the ambient temperature. The product benzyl alcohol was obtained after evaporation of all volatiles (THF, CH₃OH) under vacuum. The results are shown in tables 1-4 below. See table 2 for a complete list of tested substrates.

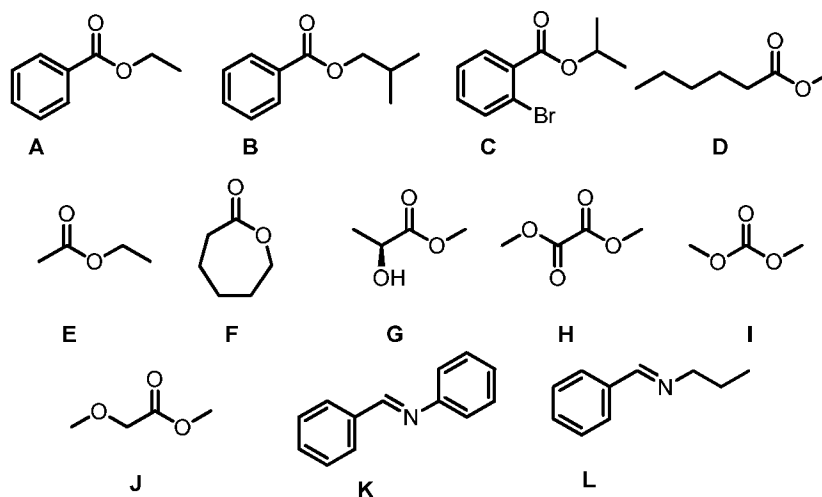
Table 1. Hydrogenation of methyl benzoate catalyzed by complexes **1** - **3**, **7** and **9** ^[a]

Entry	Catalyst	Ester/[M] ^[b]	T, °C	Time, h	Conv., %
1	1 ^[c]	2000	100	1.5	100
2	2	2000	40	22	28
3	2	2000	60	7	82
4	2	2000	80	2.2	76
5	2	2000	100	1.5	99
6	2	3000	100	3	100
7	2	10000 ^[d]	100	19	80
8	3 ^[c]	2000	100	1.7	100
9	9	2000	40	17	82
10	9	2000	60	2.2	71
11	9	2000	80	1.2	88
12	9	2000	100	1	99
13	9	10000	100	14	100
14	9	20000	100	17	90
15	7	4000	40	16	98

[a] 20 mmol of PhCOOMe in 7 mL of THF was hydrogenated in a 75 mL Parr pressure vessel.

[b] Substrate to metal molar ratio. [c] With 1 mol% of *t*BuOK. [d] 120 mmol of PhCOOMe, in a 300 mL vessel.

Table 2. Hydrogenation of esters (A-J) and imines (K, L) that afforded the corresponding alcohols and amines, catalyzed by complexes **2**, **7** and **9**^[a].



Entry	Ester	Catalyst	Ester/[M] ^[b]	Temp., °C	Time, h	Conv., %
1	A	2	2000	100	1.6	99
2	B	2	2000	100	1.5	93
3	C	2	2000	100	17	0
4	D	2	2000	100	2	100
5	D	2 ^[c]	3000	100	2.7	100
6	D	9	2000	100	1.5	93
7	D	9	10000	100	18	71
8	D	7 ^[d]	20000	40	18	94
9	E	2	2000	100	3	100
10	E	7 ^[e]	20000	40	16	100
11	F	2	2000	100	1.4	99
12	F	9	2000	100	5	67
13	G	2	2000	100	9	72
14	G	7 ^[f]	2000	40	16	98
15	H	2	2000	100	23	0
16	I	9	2000	100	5.7	85
17	J	7 ^[g]	4000	40	16	100
18	K	7 ^[g]	50000	40	16	100
19	L	7 ^[g]	2000	40	16	100

[a] 20 mmol of substrate in 7 mL of THF was hydrogenated in a 75 mL pressure vessel under $p(\text{H}_2) = 50$ Bar. [b] Substrate to metal molar ratio. [c] 120 mmol of substrate, using a 300 mL vessel. [d] With 5 mol% of KOMe. [e] With 1 mol% of NaOEt. [f] With 10 mol% of KOMe. [g] With 1 mol% of *t*BuOK.

Table 3. Exemplary Substrate - Product pairs

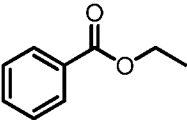
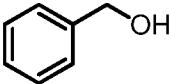
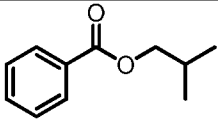
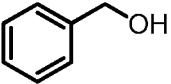
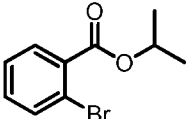
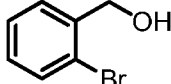
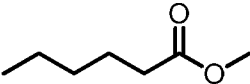
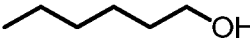
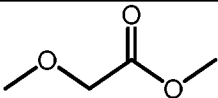
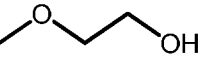
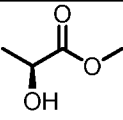
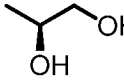
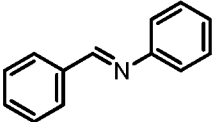
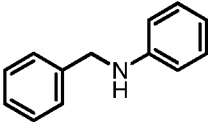
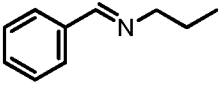
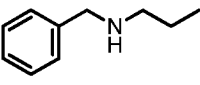
Substrate	Product
	 + EtOH
	 + tBuOH
	 + iPrOH
	 + MeOH
	 + MeOH
	 + MeOH
	
	

Table 4. Hydrogenation of fatty esters catalyzed by complexes **2**, **3** and **9**^[a]

Substrate	[cat], $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{OR}'/[\text{M}]$	Product	Conversion
	2 , 2000 THF, 16 h		100%
	3 ^[a] , 2000 THF, 16 h		100%
	2 , 2000 THF, 6 h		100%
	9 , 2000 THF, 4 h		
		N/R	0%
	2 , 2000 THF, 4 h		99%
	9 , 1000 THF, 14 h		8%
			32%
			60%
	2 , 1000 Toluene, 6.5 h		98%
Extra-virgin olive oil ^[b]	2 , 1000 Toluene, 6.5 h		ca. 90%
	2 , 3000 Toluene, 19 h		
		(ca. 85%)	

[a] with tBuOK, 0.5 mol%. [b] A mixture of triglycerides of oleic (ca. 85%), linoleic (ca. 2-3%), and palmitic acids as the main components in our samples.

[0082] Example 8 - Hydrogenation of methyl benzoate using complex 2

[0083] 1 mL of a solution containing 4.7 mg/mL of **2** (0.01 mmol [Os]) in THF or toluene was added to a solution of methyl benzoate (2.72 g, 20.0 mmol) in 6 mL of THF or toluene. The subsequent manipulations were carried out following the procedure in Example 7.

[0084] Example 9 - Hydrogenation of olive oil using complex 2

[0085] 0.6 mL of a 4.7 mg/mL solution of **2** in toluene (containing 0.006 mmol [Os]) was added to a solution of olive oil (1.86 g, 2.00 mmol) in 6 mL of toluene. All subsequent manipulations were carried out following the procedure in Example 7 using a 7 h reaction time. The product mixture was evaporated and dried under vacuum for 1 h. Further separation of the fatty alcohol from glycerol could be performed by hexane extraction or by centrifugation and decantation of the fatty alcohol from glycerol.

[0086] Example 10 - Hydrogenation of methyl caproate using complex 3

[0087] 1 mL of a 4.2 mg/mL solution of **3** (0.01 mmol) in THF or toluene and *t*BuOK (22.6 mg, 0.2 mmol) were added to a solution of methyl caproate (2.94 g, 20.0 mmol) in 6 mL of THF or toluene. All subsequent manipulations were carried out following the procedure described in Example 7.

[0088] Example 11 – Synthesis of $\text{NH}_2(\text{CH}_2)_2\text{PPh}_2$

[0089] In a 500 mL flask, 50.0 g (0.191 mol) of PPh_3 was dissolved in 200 mL of THF and 4.00 g (0.571 mol) of granulated Li was added. The mixture rapidly changed color to bright-orange, then to dark-red. The reaction was stirred overnight, and then the product solution was filtered through a glass frit into a 500 mL flask. Slow addition of 19.3 g (0.166 mol) of 2-chloroethylamine hydrochloride to the filtrate (Caution: Exothermic reaction!) afforded a light-orange solution that was left to stir for an additional 30 min and then was treated with 3.00 g of H_2O . Solvent removal under vacuum afforded a viscous residue. The crude product was washed with 3×20 mL of hexane and the remaining white slurry was extracted with 70 mL of toluene and filtered through a short plug (2 cm $\times$ 1 cm) of Al_2O_3 . The toluene extract was evaporated using a rotavap and subsequently dried under vacuum to give 34.69 g (91 %) of crude (83-85 %)

$\text{NH}_2(\text{CH}_2)_2\text{PPh}_2$ as a light-yellow oil. This product was used without purification in the synthesis of Example 12.

[0090] Example 12 - Synthesis of $\text{PyCH}=\text{NCH}_2\text{CH}_2\text{PPh}_2$

[0091] A solution of 2-picolyl aldehyde (23.2 g, 0.216 mol) in 20 mL of THF was slowly added to 60 g (83%, 0.218 mol) of 2-aminoethyl diphenylphosphine in 80 mL of THF and the mixture was stirred for 3 h. Then, 40 mL of hexane was added and the mixture was left in a refrigerator at -18°C , which produced an off-white precipitate. The solid was filtered off, washed with denatured ethanol (2×10 mL) and 40 mL of hexane, and then dried under vacuum for 2 h. The product was obtained as an off-white solid. Yield 47.2 g (68 %).

[0092] ^1H NMR ([D6]Benzene) $\delta = 8.54 - 8.33$ (m, 2H, Py+NCH), 8.09 (dd, $J=7.9$, 1.0 Hz, 1H, Py), 7.54 – 7.32 (m, 4H, Ph), 7.12 – 6.99 (m, 7H, Ph+Py), 6.71 – 6.53 (m, 1H, Py), 3.79 – 3.55 (m, 2H, CH_2), 2.46 – 2.24 (m, 2H, CH_2). ^{13}C NMR ([D6]Benzene) $\delta = 162.70$ (s, 1C, Py), 155.78 (s, 1C, N=C), 149.64 (s, 1C, Py), 139.56 (d, $J(\text{CP})=14.3$ Hz, 2C, {ArP} C^{ipso}), 136.05 (s, 1C, Py), 133.30 (d, $J(\text{CP})=19.0$ Hz, 4C, {ArP} C^{ortho}), 128.87 (s, 2C, {Ar} C^{para}), 128.78 (s, 4C, {Ar} C^{meta}), 124.53 (s, 1C, Py), 121.04 (s, 1C, Py), 58.45 (d, $J(\text{CP})=20.3$ Hz, 1C, NCH_2), 30.50 (d, $J(\text{CP})=13.9$ Hz, 1C, CH_2P). ^{31}P NMR ([D6]Benzene) $\delta = -18.19$ (s).

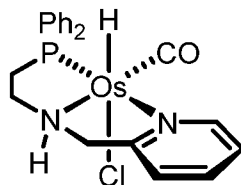
[0093] Example 13 - Synthesis of $\text{PyCH}_2\text{NH}(\text{CH}_2)_2\text{PPh}_2$

[0094] 40 g (0.126 mol) of $\text{PyCH}=\text{NCH}_2\text{CH}_2\text{PPh}_2$ was suspended in 100 mL of methanol in a 250 mL flask, followed by slow addition of 5.24 g (0.138 mol) of NaBH_4 over a 2 h period of time. After further stirring for 30 min, the mixture was evaporated and the oily residue was extracted with 3×30 mL of toluene. The toluene solution was filtered through a short plug of Al_2O_3 (2 cm $\times$ 2 cm), using additional 2×20 mL of toluene to wash the solids. The solvent was removed under vacuum and the product was dried for an additional 2 h to yield 37.2 g (92 %) of a pale-yellow oil that crystallized upon further standing (after 7 - 10 days) at room temperature.

[0095] ^1H NMR ([D6]Benzene) $\delta = 8.46$ (ddd, $J=4.8$, 1.7, 1.0 Hz, 1H, Py), 7.53 – 7.31 (m, 4H, Ph), 7.12 – 6.91 (m, 6H, Ph), 6.62 (ddd, $J=7.2$, 4.8, 1.5 Hz, 1H, Py), 3.79 (s, 2H, CH_2), 2.75 (dd, $J=15.2$, 8.5 Hz, 2H, CH_2), 2.25 – 2.02 (m, 2H, CH_2), 1.67 (br. s, 1H, NH). $^{13}\text{C}\{^1\text{H}\}$ NMR ([D6]Benzene) $\delta = 161.06$ (s, 1C, Py), 149.48 (s, 1C, Py), 139.74 (d, $J(\text{CP})=14.2$ Hz, 2C,

{ArP}C^{ipso}), 135.84 (s, 1C, Py), 133.18 (d, $J(\text{CP})=18.8$ Hz, 4C, {ArP}C^{ortho}), 128.69 (d, $J(\text{CP})=6.5$ Hz, 4C, {ArP}C^{meta}), 128.62 (s, 2C, {ArP}C^{para}), 121.94 (s, 1C, Py), 121.61 (s, 1C, Py), 55.39 (s, 1C, CH₂N), 46.79 (d, $J(\text{CP})=20.7$ Hz, 1C, NCH₂), 29.79 (d, $J(\text{CP})=12.9$ Hz, 1C, CH₂P).

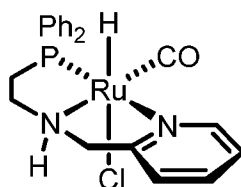
[0096] Example 14 - Synthesis of *trans*-OsHCl(CO)[PyCH₂NH(CH₂)₂PPh₂]



Complex 4

[0097] A flask containing a mixture of OsHCl(CO)(AsPh₃)₃ (3.00 g, 2.56 mmol) and PyCH₂NH(CH₂)₂PPh₂ (0.818 g, 2.56 mmol) in 30 mL of diglyme was placed in an oil bath preheated to 160 °C, and stirred for 3 h affording a dark-red solution. After cooling to room temperature, the mixture was diluted with 30 mL of hexane, and the flask was stored for 1 h in a freezer at -23 °C. The precipitated product was filtered off, washed with diethyl ether (3 × 5 mL), and recrystallized from 20 mL DCM:Et₂O mixture (3:1). Yield: 779 mg (53 %).

[0098] ¹H{³¹P} NMR ([D₂]DCM) δ = 9.04 (d, $J=5.1$ Hz, 1H, Py), 7.81 – 7.59 (m, 5H, Ph+Py), 7.45 – 7.30 (m, 6H, Ph), 7.28 – 7.16 (m, 2H, Py), 4.64 (dd, $J=14.6, 4.4$ Hz, 1H, CH₂), 4.50 (br t, $J=11.5$ Hz, 1H, NH), 3.96 (dd, $J=14.1, 11.7$ Hz, 1H, CH₂), 3.80 – 3.67 (m, 1H, CH₂), 3.09 (dd, $J=14.5, 1.9$ Hz, 1H, CH₂), 2.74 (dtd, $J=14.7, 11.6, 3.3$ Hz, 1H, CH₂), 2.32 (td, $J=14.6, 5.4$ Hz, 1H, CH₂), -15.81 (s, 1H, OsH). ¹³C{¹H} NMR ([D₂]DCM) δ = 188.19 (dd, $J(\text{CP})=9.2, 5.6$ Hz, residual coupling with OsH, 1C, CO), 161.63 (s, 1C, Py), 154.20 (d, $J(\text{CP})=1.5$ Hz, 1C, Py), 139.78 (d, $J(\text{CP})=54.6$ Hz, 1C, {Ar}C^{ipso}), 136.70 (s, 1C, Py), 135.90 (d, $J(\text{CP})=50.4$ Hz, 1C, {Ar}C^{ipso}), 133.61 (d, $J(\text{CP})=10.9$ Hz, 1C, 2C, {Ar}C^{ortho}), 132.69 (d, $J(\text{CP})=10.8$ Hz, 2C, {Ar}C^{ortho}), 130.50 (d, $J(\text{CP})=2.4$ Hz, 1C, {Ar}C^{para}), 130.36 (d, $J(\text{CP})=2.4$ Hz, 2C, {Ar}C^{para}), 128.82 (d, $J(\text{CP})=10.4$ Hz, 2C, {Ar}C^{meta}), 128.66 (d, $J(\text{CP})=10.4$ Hz, {Ar}C^{meta}), 125.34 (d, $J(\text{CP})=2.0$ Hz, Py), 122.02 (d, $J(\text{CP})=1.5$ Hz, Py), 60.63 (s, 1C, PyCH₂), 53.73 (d, $J(\text{CP})=2.1$ Hz, 1C, NCH₂), 35.91 (d, $J(\text{CP})=30.8$ Hz, 1C, CH₂P). ³¹P{¹H} NMR ([D₂]DCM) δ = 29.7 (s).

[00099] Example 15 - Synthesis of *trans*-RuHCl(CO)[PyCH₂NH(CH₂)₂PPh₂]

Complex 5

[00100] A 50 mL Schlenk flask containing a mixture of RuHCl(CO)(AsPh₃)₃ (5.73 g, 4.68 mmol) and PyCH₂NH(CH₂)₂PPh₂ (1.5 g, 4.68 mmol) in 30 mL of dioxane was stirred under reflux for 3 h affording a dark brown solution. After cooling to room temperature, the mixture was diluted with 5 mL of Et₂O and left in a refrigerator at -15 °C. The crystallized product was filtered, then washed with diethyl ether (2 × 5 mL), and dried under vacuum. Yield: 1.71 g (75 %) of a grey solid.

[00101] ¹H{³¹P} NMR ([D₂]DCM) δ = 8.97 (d, *J*=5.4 Hz, 1H, Py), 7.95 – 7.55 (m, 5H, Ph+Py), 7.47 – 7.35 (m, 6H, Ph), 7.33 – 7.26 (m, 1H, Py), 7.22 (d, *J*=7.8 Hz, 1H, Py), 4.45 (dd, *J*=15.3, 4.2 Hz, 2H, PyCH₂), 4.09 (dd, *J*=15.3, 12.7 Hz, 1H, CH₂), 3.71 – 3.51 (br, 1H, NH), 3.00 (dd, *J*=14.1, 1.8 Hz, 1H, CH₂), 2.75 (dtd, *J*=14.3, 11.3, 3.1 Hz, 1H, CH₂), 2.53 (td, *J*=14.4, 5.1 Hz, 1H, CH₂), -14.30 (s, 1H, RuH). ¹³C{¹H} NMR ([D₂]DCM) δ = 205.80 (d, *J*(CP)=17.9 Hz), 160.84 (s, 1C, Py), 153.92 (d, *J*(CP)=1.1 Hz, 1C, Py), 138.73 (d, *J*(CP)=49.5 Hz, 1C, {Ar}C^{ipso}), 137.14 (s, 1C, Py), 135.66 (d, *J*(CP)=43.7 Hz, 1C, {Ar}C^{ipso}), 133.46 (d, *J*(CP)=11.0 Hz, 2C, {Ar}C^{ortho}), 132.62 (d, *J*(CP)=11.4 Hz, 2C, {Ar}C^{ortho}), 130.44 (d, *J*(CP)=2.4 Hz, 1C, {Ar}C^{para}), 130.34 (d, *J*(CP)=2.3 Hz, 1C, {Ar}C^{para}), 128.84 (d, *J*(CP)=10.1 Hz, 2C, {Ar}C^{meta}), 128.61 (d, *J*(CP)=10.1 Hz, 2C, {Ar}C^{meta}), 124.61 (d, *J*(CP)=2.2 Hz, 1C, Py), 121.75 (d, *J*(CP)=1.6 Hz, 1C, Py), 59.77 (d, *J*(CP)=1.5 Hz, 1C, CH₂), 51.92 (d, *J*(CP)=4.1 Hz, 1C, CH₂), 35.14 (d, *J*(CP)=26.0 Hz, 1C, CH₂). Anal. Calcd for C₂₀H₂₁ClN₂ORuP: C, 47.23; H, 6.61; N, 7.34. Found: C, 46.95; H, 6.53; N, 7.15.

[00102] Example 16 - Typical Procedure for Acceptorless Alcohol Dehydrogenation

[00103] A 50 mL Schlenk flask equipped with a stir bar was charged with 0.052 mmol of Complex **2**, **3**, or **5**, 0.5 – 1 mol% of *t*BuOK (with **3** and **5**), and the calculated amount of

substrate (1000:1, substrate to metal ratio) under argon. Then, the flask (attached to and vented through an argon manifold) was placed in an oil bath, where it was heated at a temperature slightly exceeding the boiling point of the neat alcohol. The conversion was monitored by ¹H NMR spectroscopy using 0.6 mL samples retrieved from the reaction solutions through the septum stopper with the help of a syringe.

Table 5. Results of catalytic acceptorless dehydrogenation of alcohols.

Entry	R ^[a]	T, °C	cat	ROH/[M] ^[b]	t, h	Conversion, %
1	Me	78	5 ^[e]	1000	7.5	9
2	Me	78	5 ^[c,e]	1000	19	25
3	Me	78	2	1000	24	7
4	Me	78	2 ^[c]	1000	8	61
5	Me	78	2 ^[c,d]	1000	8	96
6	Me	78	3 ^[d]	1000	7.5	30
7	Me	78	7 ^[f]	2000	16	95
8	Me	78	7 ^[g]	10000	24	91
9	Me	78	7 ^[g]	20000	40	85
10	Me	78	7 ^{[f][h]}	2000	16	89
11	Et	96	5 ^[e]	1000	6	69
12	Et	96	2	1000	8.5	86
13	Et	96	3 ^[d]	1000	8	73
14	Pr	118	5 ^[e]	1000	2	73
15	Pr	118	2	1000	3	93
16	Pr	118	3 ^[d]	1000	3	78
17	<i>i</i> -Amyl	131	5 ^[e]	1000	2.5	88
18	<i>i</i> -Amyl	131	2	1000	3	86
19	<i>i</i> -Amyl	131	3 ^[d]	1000	2.5	92

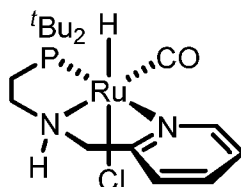
Entry	R ^[a]	T, °C	cat	ROH/[M] ^[b]	t, h	Conversion, %
20	Hexyl	158	5 ^[e]	1000	2	86
21	Hexyl	158	2	1000	1.3	97
22	Hexyl	158	2	4000	1.3	71
23	Hexyl	158	3 ^[d]	1000	1	86

[a] Using 52 mmol of neat substrate and 1 mol% of EtONa for catalyst **7**. [b] Substrate to metal molar ratio. [c] In toluene. [d] With 0.5 mol% of *t*BuOK. [e] With 1 mol% of *t*BuOK. [f] Using 0.1 mol of neat substrate. [g] Using 0.2 mol of neat substrate. [h] Reaction was prepared in air using standard anhydrous grade ethanol

[00104] Example 17 - Synthesis of PyCH₂NH(CH₂)₂P*t*Bu₂

[00105] The synthesis of NH₂(CH₂)₂P*t*Bu₂ was performed following a known procedure (6, incorporated herein by reference). A solution of 2-picolyl aldehyde (2.04 g, 19.04 mmol) in 10 mL of THF was added to 2-(di-*tert*-butylphosphino)ethylamine (3.60 g, 19.04 mmol) in 10 mL of THF. The mixture was stirred for 1 h, then evaporated and dried for 1 h under vacuum. The oily residue was re-dissolved in 15 mL of toluene and was slowly (over a period of 1 h) treated with 1.5M solution of DIBAL in toluene (16.5 mL, 24.75 mmol) (Caution: exothermic reaction!). The product solution was stirred for 30 min, and then quenched with 1 mL of water (Caution: exothermic reaction!). The resulting suspension was filtered through a short plug (2.1 cm) of basic alumina and the solids were washed with THF (3×10 mL). The filtrate was evaporated and dried under vacuum for 3 h to give the product as a yellow oil (3.79 g, 71 %).

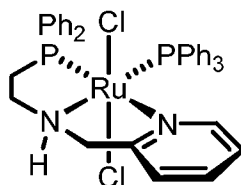
[00106] ¹H{³¹P} NMR ([D₆]Benzene) δ = 8.49 (d, *J* = 4.8 Hz, 1H, Py), 7.19 – 7.15 (m, 1H, Py overlapped with C₆D₅H), 7.10 (t, *J* = 7.1 Hz, 1H, Py), 6.64 (dd, *J* = 6.3, 5.8 Hz, 1H, Py), 3.96 (s, 2H, PyCH₂), 2.87 (t, *J* = 7.7 Hz, 2H, NCH₂), 1.91 (br, 1H, NH) 1.56 (t, *J* = 7.7 Hz, 2H, CH₂P), 1.07 (s, 18H, CH₃). ¹³C{¹H} NMR ([D₆]Benzene) δ = 161.46 (s, 1C, Py), 149.48 (s, 1C, Py), 135.84 (s, 1C, Py), 121.91 (s, 1C, Py), 121.58 (s, 1C, Py), 55.79 (s, 1C, CH₂), 50.78 (d, *J*(CP) = 34.2 Hz, 1C, CH₂), 31.19 (d, *J*(CP) = 22.1 Hz, 2C, CMe₃), 29.82 (d, *J*(CP) = 14.0 Hz, 6C, CH₃), 22.96 (d, *J*(CP) = 27.5 Hz, 1C, CH₂P). ³¹P{¹H} NMR ([D₆]Benzene) δ = 20.47 (s).

[00107] Example 18 - Synthesis of *trans*-RuHCl(CO)[PyCH₂NH(CH₂)₂P*t*Bu₂]

Complex 6

[00108] A mixture of RuHCl(CO)(AsPh₃)₃ (1.93 g, 1.79 mmol) and PyCH₂NH(CH₂)₂P*t*Bu₂ (500 mg, 1.79 mmol) in 10 mL of diglyme was stirred for 3 h at 140 °C in a 50 mL Schlenk flask. After cooling to room temperature, 2 mL of Et₂O was added, and the mixture was left to crystallize at −18 °C. The product was filtered, washed with diethyl ether (2×3 mL), and dried under vacuum to give a grey solid. Yield: 431 mg (54 %).

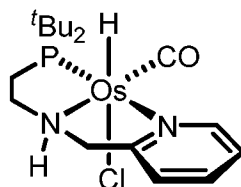
[00109] ¹H{³¹P} NMR ([D₂]DCM) δ = 8.89 (dt, *J* = 5.4, 0.8 Hz, 1H; Py), 7.66 (td, *J* = 7.7, 1.6 Hz, 1H; Py), 7.22 (dd, *J* = 15.5, 7.2 Hz, 2H; Py), 4.68 (br., 1H; NH), 4.45 (dd, *J* = 15.0, 4.7 Hz, 1H; CH₂), 4.00 (dd, *J* = 14.9, 11.5 Hz, 1H; CH₂), 3.61 – 3.44 (m, 1H; CH₂), 2.67 (dtd, *J* = 13.4, 11.6, 4.8 Hz, 1H; CH₂), 2.26 (dd, *J* = 14.7, 4.2 Hz, 1H; CH₂), 2.07 (td, *J* = 14.2, 6.4 Hz, 1H; CH₂), 1.35 (d, *J* = 5.3 Hz, 18H; CH₃), −15.59 (s, 1H; RuH). ¹³C{¹H} NMR ([D₂]DCM) δ 206.49 (dd, *J*(CP) = 15.5, *J*(CH) = 6.9 Hz residual coupling with OsH, 1C; CO), 160.73 (s, 1C; Py), 153.59 (s, 1C; Py), 136.74 (s, 1C; Py), 124.37 (d, *J*(CP) = 1.6 Hz, 1C; Py), 121.33 (s, 1C; Py), 52.51 (s, 1C; CH₂), 38.29 (d, *J*(CP) = 15.0 Hz, 1C; CH₂), 37.55 (d, *J*(CP) = 24.6 Hz, 1C; CMe₃), 37.52 (d, *J*(CP) = 24.6 Hz, 1C; CMe₃), 30.93 (d, *J*(CP) = 4.3 Hz, 3C; CH₃), 30.07 (d, *J*(CP) = 3.2 Hz, 3C; CH₃), 28.49 (d, *J*(CP) = 14.9 Hz, 1C; PCH₂). ³¹P{¹H} NMR ([D₂]DCM) δ 106.10 (s). Anal. Calcd for C₁₇H₃₁ClN₂OPRu: C, 45.68; H, 6.99; N, 6.27. Found: C, 45.40; H, 6.74; N, 5.92.

[00110] Example 19 - Synthesis of *trans*-RuCl₂(PPh₃)₂[PyCH₂NH(CH₂)₂PPh₂]

Complex 7

[00111] Stirring a mixture of RuCl₂(PPh₃)₃ (4.20 g, 4.38 mmol) and PyCH₂NH(CH₂)₂PPh₂ (1.40 g, 4.38 mmol) in 30 mL of toluene (or 1,4-dioxane) for 3 h at 40 °C in a 100 mL Schlenk flask produced a yellow suspension. The product was filtered in air, washed with 10 mL of Et₂O, and dried under vacuum for 2 h to give a yellow solid. Yield: 3.1 g (94 %).

[00112] ¹H{³¹P} NMR ([D₂]DCM) δ 8.42 (d, *J* = 5.6 Hz, 1H; Py), 7.77 – 7.53 (m, 3H), 7.53 – 6.91 (m, 29H), 6.85 (t, *J* = 6.6 Hz, 1H; Py), 5.49 (t, *J* = 13.0 Hz, 1H; CH₂), 5.23 (br, 1H; NH), 4.28 (dd, *J* = 13.9, 3.5 Hz, 1H; CH₂), 3.66 – 3.31 (m, 2H; CH₂), 2.91 – 2.57 (m, 2H; CH₂), 2.35 (s, 3H; CH₃Tol). ¹³C{¹H} NMR ([D₂]DCM) δ 163.50 (s, 1C; Py), 156.81 (s, 1C; Py), 139.44 (d, *J* = 32.2 Hz, 2C; {PPh₂}C^{ipso}), 137.89 (s, 1C; Py), 137.13 (d, *J*(CP) = 39.3, 3C; {PPh₃}C^{ipso}), 135.95 – 135.29 (m, 6C; {PPh₃}C^{ortho}), 135.11 (d, *J*(CP) = 8.4 Hz, 2C; {PPh₂}C^{ortho}), 134.47 (d, *J*(CP) = 9.1 Hz, 2C; {PPh₂}C^{ortho}), 129.38 (d, *J*(CP) = 4.5 Hz, 2C; {PPh₂}C^{para}), 129.38 (s, 3C; {PPh₃}C^{para}), 128.48 – 127.05 (m, 10C; {PPh₂}C^{meta}+{PPh₃}C^{meta}), 122.96 (s, 1C; Py), 121.92 (s, 1C; Py), 67.59 (s, 1,4-dioxane), 57.77 (s, 1C; CH₂), 49.09 (s, 1C; CH₂), 38.77 (d, *J*(CP) = 27.4 Hz, 1C; CH₂). ³¹P{¹H} NMR ([D₂]DCM) δ 49.13 (d, *J*(PP) = 28.9 Hz, 1P), 47.39 (d, *J*(PP) = 29.0 Hz, 1P). Anal. Calcd for C₃₈H₃₆Cl₂N₂P₂Ru·C₇H₈: C, 63.83; H, 5.24; N, 3.31. Found: C, 63.23; H, 5.22; N, 3.34.

[00113] Example 20 - Synthesis of *trans*-OsHCl(CO)[PyCH₂NH(CH₂)₂P^{*t*}Bu₂]

Complex 8

[00114] A mixture of OsHCl(CO)(AsPh₃)₃ (1.675 g, 1.43 mmol) and PyCH₂NH(CH₂)₂P*t*Bu₂ (400 mg, 1.43 mmol) in 10 mL of diglyme was stirred for 3 h at 140 °C in a 50 mL Schlenk flask. After cooling to room temperature, 2 mL of Et₂O was added, and the product crystallized upon standing at -15 °C. The yellow solid was filtered, washed with diethyl ether (2×3 mL) and dried under vacuum. Yield: 507 mg (66 %).

[00115] ¹H{³¹P} NMR ([D₂]DCM) δ 8.97 (dt, *J* = 6.3, 1.4 Hz, 1H; Py), 7.67 (td, *J* = 7.8, 1.5 Hz, 1H; Py), 7.27 – 7.05 (m, 2H; Py), 4.65 (dd overlapping with br. s, *J* = 15.8, 4.7 Hz, 2H; CH₂ + NH), 3.88 (dd, *J* = 15.8, 12.2 Hz, 1H; CH₂), 3.69 – 3.43 (m, 1H; CH₂), 2.64 (ddd, *J* = 25.1, 11.4, 4.6 Hz, 1H; CH₂), 2.33 (dt, *J* = 29.2, 14.5 Hz, 1H; CH₂), 1.99 (td, *J* = 14.4, 6.4 Hz, 1H; CH₂), 1.35 (s, 18H; CH₃), -17.35 (s, 1H; OsH). ¹³C{¹H} NMR ([D₂]DCM) δ 188.49 (dd, *J*(CP) = 8.3, *J*(CH) = 4.3 Hz residual coupling with OsH, 1C; CO), 161.44 (s, 1C; Py), 153.79 (d, *J*(CP) = 1.7 Hz, 1C; Py), 136.22 (s, 1C; Py), 125.08 (d, *J*(CP) = 1.8 Hz, 1C; Py), 121.55 (d, *J*(CP) = 1.6 Hz, 1C; Py), 54.22 (s, 1C; CH₂), 39.63 (d, *J*(CP) = 20.8 Hz, 1C; CH₂), 38.96 (d, *J*(CP) = 29.1 Hz, 2C; CMe₃), 30.90 (d, *J*(CP) = 3.9 Hz, 3C; CH₃), 29.78 (d, *J*(CP) = 2.6 Hz, 3C; CH₃), 29.22 (d, *J*(CP) = 19.8 Hz, 1C; CH₂). ³¹P{¹H} NMR ([D₂]DCM) δ 62.79 (s). Anal. Calcd for C₁₇H₃₁ClN₂OPOs: C, 38.16; H, 5.65; N, 5.24. Found: C, 38.04; H, 5.72; N, 4.97.

[00116] Example 21 - Imine and ester hydrogenation using complex 7

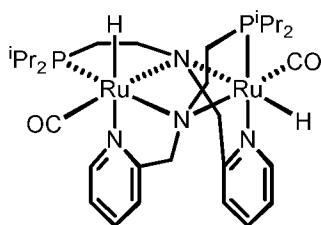
[00117] Complex 7 was further tested in hydrogenation of compounds with polar C=X bonds. There has been much recent interest in the catalytic hydrogenation of esters. Although the performance of the “state of the art” industrial catalysts is impressive, further improvements are highly desirable to (a) reduce the reaction temperature, preferably to as low as 20–40 °C, and (b) reduce the catalyst loading, preferably to less than 0.05 mol %. Guided by these considerations, complex 7 was tested in the hydrogenation of several benchmark substrates, shown in tables 1-4, above. Note that all of the reactions shown were performed at 40 °C.

[00118] In an argon glovebox, the required amount of a 1.9 mg/g solution of 4 in THF was added to the desired amount of base (*t*BuOK, MeOK, or EtOK). The obtained mixture was then mixed with the substrate (0.02 – 0.20 mol) and transferred into a stainless-steel Parr reactor (75 mL or 300 mL) equipped with a magnetic stir bar. The reactor was closed, taken out of the glovebox, tightened and connected to a hydrogen tank. After purging the line, the reactor was

pressurized to 725 psi (50 Bar) and disconnected from the H₂ source (with the exception of reactions conducted in the 300 mL reactor using 0.2 mol of substrate). Then, the reactor was placed in an oil bath preheated to 40 °C. At the end of the reaction time, the reactor was moved into a cold water bath for 5 min and depressurized.

[00119] The results of the above hydrogenation experiments demonstrate that an outstanding ethanol dehydrogenation catalyst might also have superior efficiency in hydrogenation of substrates with polar C=X bonds. Catalyst **7** is particularly successful for the reduction of alkanoates, giving an unprecedented 20 000 turnovers in 16 h for ethyl acetate and 18 800 turnovers in 18 h for methyl hexanoate, both at 40 °C. The best turnover number (TON) reported to date for this type of substrate was 7100 in 18 h at 100 °C for methyl hexanoate, using a ruthenium dimer {RuH(CO)[N(C₂H₄PiPr₂)₂]}₂ (Spasyuk, D., Smith, S., Gusev, D. G. *Angew. Chem., Int. Ed.* 2012, 51, 2772–2775). For another comparison, the best Firmenich catalyst, RuCl₂(H₂NC₂H₄PPh₂)₂, would theoretically need 27 h to produce 18 600 turnovers for methyl octanoate at 100 °C, on the basis of the reported TOF = 688 h⁻¹ over a 2.5 h reaction time. (United States patent application publication No. US 2010-280273). Complex **7** is also a competent imine hydrogenation catalyst, giving a particularly high TON = 50 000 for *N*-benzylaniline.

[00120] Example 22 - Synthesis of μ^N -{RuH(CO)[PyCH₂N(CH₂)₂P(*i*Pr)₂]}₂



Complex 9

[00121] A mixture of diethyl ether and THF (2:1, 15 mL) was added to a mixture of Complex **3** (640 mg, 1.53 mmol) and *t*BuOK (172 mg, 1.53 mmol) and the resulting solution was stirred for 5 min. During this time the color changed from yellow to dark purple, then to dark green. The product solution was placed into a freezer at -18 degrees Celsius for 15 min and subsequently filtered through a glass frit. The solvent was removed under vacuum to yield 532

mg (91%) of a mixture of two isomers of Complex 4. The major isomer was obtained in a pure form as a bright yellow solid (340 mg, 58%) after recrystallization of the mixture from 5 mL of toluene at 60 °C.

[00122] $^{31}\text{P}\{^1\text{H}\}$ NMR ([D₂]DCM) δ = 93.80 (s), 90.25 (s). $^1\text{H}\{^{31}\text{P}\}$ NMR ([D₂]DCM) δ = 9.01 (dd, J =5.5, 0.8 Hz, 1H; Py), 8.40 (d, J =5.4 Hz, 1H; Py), 7.15 (td, J =7.7, 1.6 Hz, 1H; Py), 7.10 (td, J =7.7, 1.7 Hz, 1H; Py), 6.86 (t, J =6.5 Hz, 2H; Py), 6.46 (d, J =7.9 Hz, 1H; Py), 6.27 (d, J =8.0 Hz, 1H; Py), 4.50 (d, J =18.0 Hz, 1H; CH₂), 4.15 (d, J =17.9 Hz, 1H; CH₂), 4.05 (dd, J =18.0, 1.6 Hz, 1H; CH₂), 3.55 – 3.24 (m, 3H), 3.11 (dd, J =11.8, 5.3 Hz, 1H; CH₂), 2.95 – 2.78 (m, 2H), 2.61 – 2.45 (m, 1H), 2.37 – 2.17 (m, 2H), 2.03 (dd, J =13.4, 3.8 Hz, 1H; CH₂), 1.91 (hept, J =7.2 Hz, 1H; CH), 1.74 (td, J =14.1, 5.6 Hz, 1H; CH₂), 1.53 – 1.43 (dd overlapped with d, 1H; CH₂), 1.44 (d overlapped with dd, J =7.6 Hz, 3H; CH₃), 1.38 (d, J =2.4 Hz, 3H; CH₃), 1.35 (d, J =1.8 Hz, 3H; CH₃), 1.31 (d, J =6.9 Hz, 3H; CH₃), 1.16 (d, J =6.8 Hz, 3H; CH₃), 1.05 (d, J =6.9 Hz, 6H; CH₃), 1.00 (d, J =6.8 Hz, 3H; CH₃), -12.45 (s, 1H; RuH), -13.68 (s, 1H; RuH). $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₆]Benzene) δ = 209.64 (d, $J(\text{CP})$ =17.0 Hz, 1C; CO), 207.30 (d, $J(\text{CP})$ =12.4 Hz, 1C; CO), 169.03 (d, $J(\text{CP})$ =2.2 Hz, 1C; Py), 168.09 (s, 1C; Py), 155.64 (s, 1C; Py), 151.26 (s, 1C; Py), 134.92 (s, 1C; Py), 134.51 (s, 1C; Py), 121.37 (d, $J(\text{CP})$ =2.4 Hz, 1C; Py), 120.97 (s, 1C; Py), 118.09 (s, 1C; Py), 117.65 (s, 1C; Py), 74.01 (d, $J(\text{CP})$ =2.6 Hz, 1C; PyCH₂), 71.36 (m, 2C; PyCH₂+ NCH₂), 69.73 (s, 1C; NCH₂), 33.66 (d, $J(\text{CP})$ =22.8 Hz, 1C; CH), 31.68 (d, $J(\text{CP})$ =11.5 Hz, 1C; CH), 29.39 (d, $J(\text{CP})$ =4.1 Hz, 1C; CH₂), 29.11 (s, 1C; CH₂), 26.64 (d, $J(\text{CP})$ =29.2 Hz, 1C; CH), 25.11 (d, $J(\text{CP})$ =32.6 Hz, 1C; CH), 21.60 (d, $J(\text{CP})$ =4.1 Hz, 1C; CH₃), 21.47 (d, $J(\text{CP})$ =5.1 Hz, 1C; CH₃), 21.07 (d, $J(\text{CP})$ =7.3 Hz, 1C; CH₃), 20.94 (d, $J(\text{CP})$ =5.0 Hz, 1C; CH₃), 19.77 (s, 1C; CH₃), 19.41 (s, 1C; CH₃), 17.69 (d, $J(\text{CP})$ =3.2 Hz, 1C; CH₃), 17.59 (d, $J(\text{CP})$ =2.9 Hz, 1C; CH₃). Anal. Calcd for (C₁₅H₂₅N₂RuOP)₂: C, 47.23; H, 6.61; N, 7.34. Found: C, 46.95; H, 6.53; N, 7.15.

[00123] Example 23 - Crystal Structure Determination of Complex 7

[00124] Single crystals of complex 7 were grown by slow diffusion of hexanes into a saturated solution in dichloromethane. The data was collected on a Bruker MicrostarTM generator equipped with Helios optics, a Kappa NoniusTM goniometer, and a Platinum-135 detector. Cell refinement and data reduction were done using SAINTTM (SAINT (1999) Release 6.06;

Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, Wisconsin, USA.) An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABSTM (Sheldrick, G.M. (1999). SADABS, Bruker Area Detector Absorption Corrections. Bruker AXS Inc., Madison, Wisconsin, USA.). The space group was confirmed by XPREP routine of SHELXTL (XPREP (1997) Release 5.10; X-ray data Preparation and Reciprocal space Exploration Program, Bruker AXS Inc., Madison, Wisconsin, USA.; SHELXTL (1997) Release 5.10; The Complete Software Package for Single Crystal Structure Determination, Bruker AXS Inc., Madison, Wisconsin, USA.). The structure was solved by direct-methods and refined by full-matrix least squares and difference Fourier techniques with SHELX-97 as a part of LinXTL tool box (Sheldrick, G.M. (1997). SHELXS97, Program for the Solution of Crystal Structures. Univ. Of Gottingen, Germany; Sheldrick, G.M. (1997). SHELXL97, Program for the Refinement of Crystal Structures. University of Gottingen, Germany.). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter, except those of the NH moiety and hydrides, which were positioned from residual peaks in the difference Fourier map. The collection parameters and bond distances and angles can be found in tables 5 and 6, respectively.

Table 6. Crystal Data Collection and Refinement Parameters for Complex 7

chemical formula	C ₃₈ H ₃₆ Cl ₂ N ₂ P ₂ Ru
crystal colour	Yellow
<i>F</i>_w; F(000)	754.60; 772
<i>T</i> (K)	150
wavelength (Å)	1.54178
space group	P-1
<i>a</i> (Å)	10.5195(3)
<i>b</i> (Å)	13.2513(3)
<i>c</i> (Å)	16.3644(4)
<i>α</i>(deg)	68.972(1)
<i>β</i>(deg)	88.622(1)

$\gamma(\text{deg})$	67.031(1)
Z	2.00
$V(\text{\AA}^3)$	1942.49(9)
$\rho_{\text{calcd}}(\text{g}\cdot\text{cm}^{-3})$	1.290
$\mu(\text{mm}^{-1})$	5.511
θ range (deg); completeness	4.61 – 69.76; 0.971
collected reflections; R_{σ}	30435; 0.0328
unique reflections; R_{int}	30435; 0.0386
$R1^a$; $wR2^b$ [$I > 2\sigma(I)$]	0.0297; 0.0765
$R1$; $wR2$ [all data]	0.0299; 0.0767
GOF	0.975
largest diff peak and hole	1.054 and -0.464

Table 7. Selected Bond Distances ($\text{\AA}$) and Angles (deg) for Complex 7

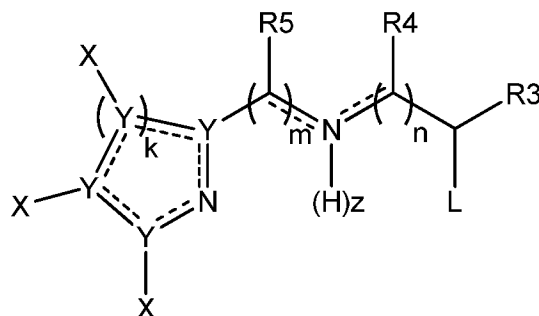
7	
Ru1-N1	2.143(2)
Ru1-N2	2.160(2)
Ru1-P1	2.302(5)
Ru1-P2	2.3305(4)
Ru1-Cl2	2.4093(4)
Ru1-Cl1	2.4138(4)
N1-Ru1-N2	75.46(6)
N1-Ru1-P1	83.43(5)
N2-Ru1-P1	158.00(4)
N2-Ru1-P2	97.93(4)
P1-Ru1-P2	103.56(2)
P1-Ru1-Cl2	95.6(2)

[00125] All publications, patents and patent applications mentioned in this Specification are indicative of the level of skill of those skilled in the art to which this invention pertains and are herein incorporated by reference to the same extent as if each individual publication, patent, or patent applications was specifically and individually indicated to be incorporated by reference.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

What is claimed is:

1. A compound of Formula I



I

wherein

L is a phosphine (PR^1R^2), a sulfide (SR^1), or a carbene group (CR^1R^2);

each Y is independently a C, N or S atom, wherein at least two Y's are C;

the dotted lines simultaneously or independently represent single or double bonds;

R^1 and R^2 are each independently H, or a C_1 - C_{20} linear alkyl, a C_3 - C_{20} branched alkyl, a C_3 - C_8 cycloalkyl, a C_2 - C_8 alkenyl, a C_5 - C_{20} aryl, each of which may be optionally substituted, or OR or NR_2 ; or when taken together, R^1 and R^2 can together with L to which they are bound form a saturated or partially saturated ring;

R^3 and R^4 are each independently H, or a C_1 - C_8 linear alkyl, a C_3 - C_8 branched alkyl, a C_3 - C_8 cyclic alkyl, a C_2 - C_8 alkenyl, a C_5 - C_8 aryl, each of which may be optionally substituted; or R^3 and R^4 can join together to form a saturated cycloalkane or saturated heterocycle;

R^5 is H, a linear C_1 - C_8 alkyl, a branched C_3 - C_8 alkyl, a cyclic C_3 - C_8 alkyl, a C_2 - C_8 alkenyl, or a C_5 - C_8 aryl, each of which can be optionally substituted; or R^5 and R^4 can join together to form a saturated heterocycle;

each X is independently H, a linear C_1 - C_8 alkyl, a branched C_3 - C_8 alkyl, a cyclic C_3 - C_8 alkyl, a C_2 - C_8 alkenyl, or a C_5 - C_8 aryl, each of which can be optionally substituted, or OR, F, Cl, Br, I or NR_2 ; or when taken together, two of the X groups can together form an optionally substituted, saturated, partially saturated, aromatic or heteroaromatic ring;

R is H, a C_1 - C_{20} linear alkyl, a C_3 - C_{20} branched alkyl, a C_3 - C_8 cycloalkyl, a C_2 - C_8 alkenyl, or a C_5 - C_8 aryl, each of which may be optionally substituted;

each n and m is independently 1 or 2;

k is 1 or 2;

and

z is 0 or 1.

2. The compound of claim 1, wherein:

R^3 and R^4 are each independently H, or C_1 - C_8 linear alkyl, C_3 - C_8 branched alkyl, cyclic alkyl C_3 - C_8 , C_1 - C_8 alkenyl, C_5 - C_8 aryl, each of which may be optionally substituted; and

R^5 is H, a linear C_1 - C_8 alkyl, branched C_3 - C_8 alkyl, cyclic C_3 - C_8 alkyl, C_3 - C_8 alkenyl, or C_5 - C_8 aryl, each of which can be optionally substituted.

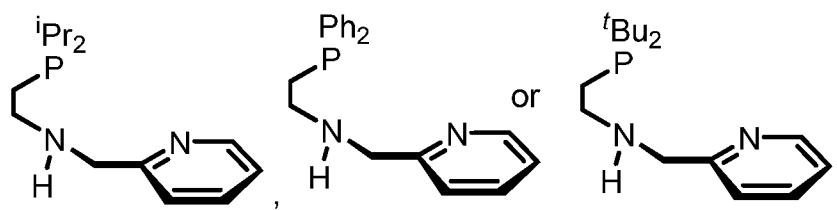
3. The compound of claim 1 or claim 2, wherein R^4 and R^5 are both H.

4. The compound of any one of claims 1-3, wherein each Y is C.

5. The compound of any one of claims 1-4, wherein k is 2, and each X is H.

6. The compound of any one of claims 1-5, wherein L is a phosphene.

7. The compound of any one of claims 1-5, wherein the compound of Formula I is



8. A complex of Formula II or III



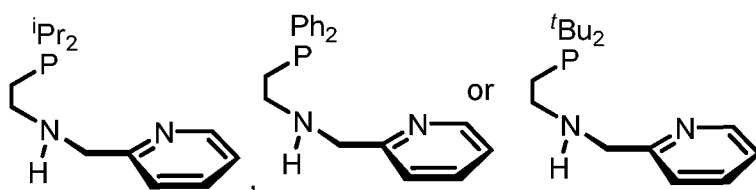
wherein:

each Z is independently a hydrogen or halogen atom, a C_1 - C_6 alkyl, a hydroxyl, or a C_1 - C_6 alkoxy, a nitrosyl (NO) group, CO, CNR, or PR_3 , wherein R is an alkyl or an aryl, PMe_3 or PPh_3 ;

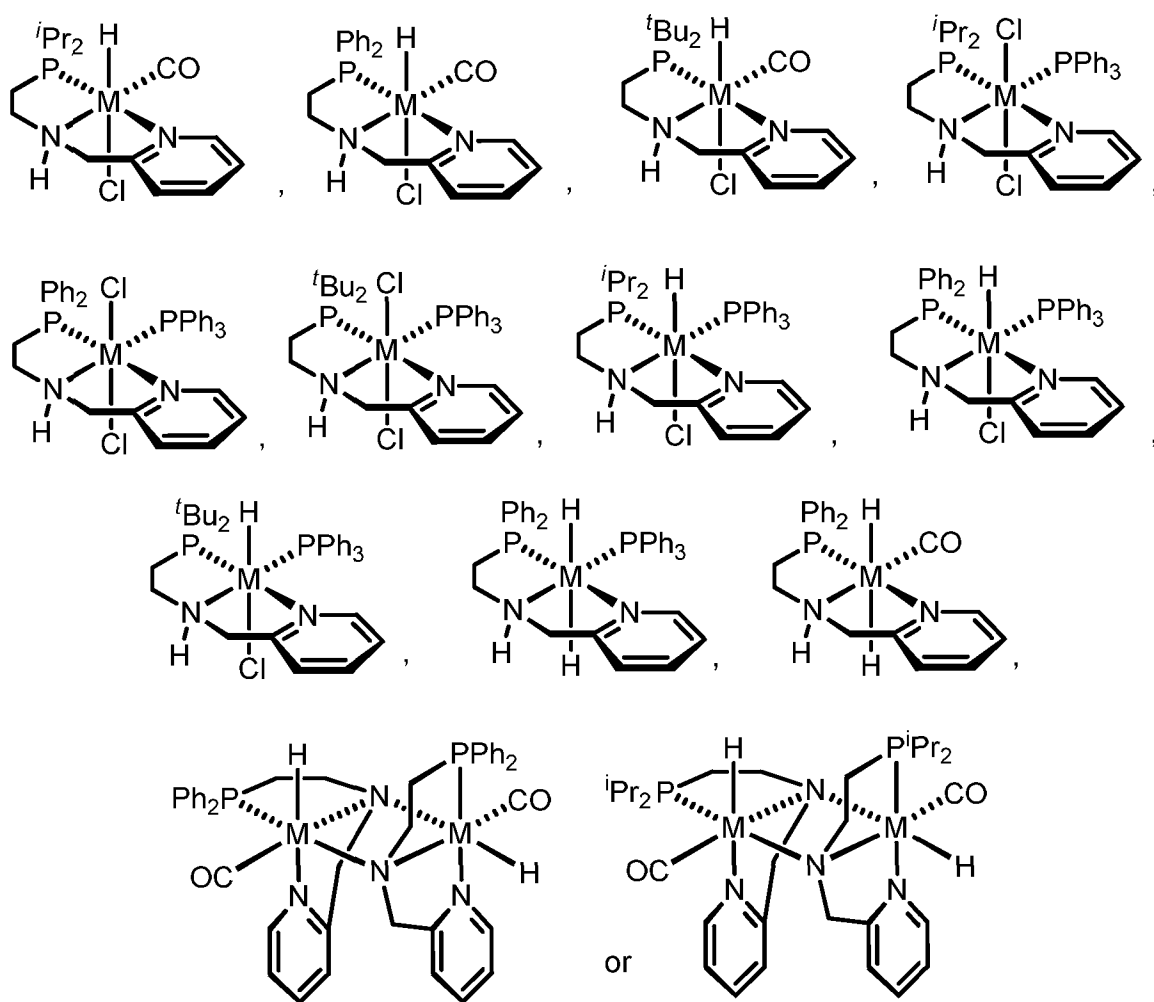
M is a transition metal; and

each LNN' is a coordinated ligand that is a compound of any one of claims 1-7.

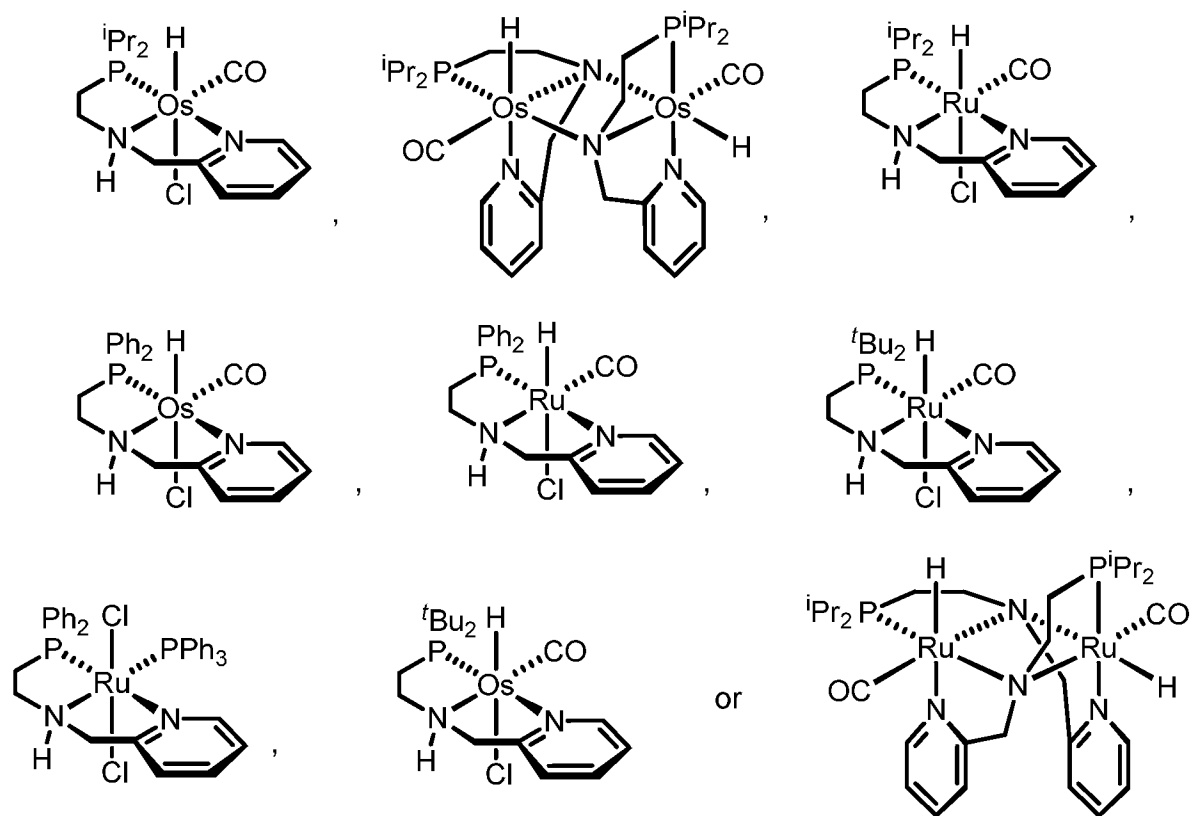
9. The complex of claim 8, wherein M is a group 7 metal, a group 8 metal or a group 9 metal.
10. The complex of claim 8 or claim 9, wherein M is Ru or Os.
11. The complex of any one of claims 8-10, wherein LNN' is



12. The complex of any one of claims 8-11 which has the structure of any one of



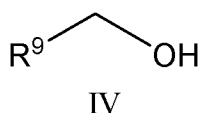
13. The complex of any one of claims 8-12, which has the structure of any one of



14. A process for dehydrogenation of a substrate comprising treating the substrate with a catalytic amount of the complex of any one of claims 8-13.

15. The process of claim 14, wherein the substrate comprises at least one alcohol moiety.

16. The process of claim 15, wherein the substrate is a compound of Formula IV



wherein R^9 is a C_{1-20} linear alkyl, a C_{3-20} branched alkyl, a C_{3-20} cycloalkyl, or an aryl, any of which may be optionally substituted.

17. The process of claim 16, wherein the compound of Formula IV comprises more than one hydroxyl moiety that can undergo dehydrogenation.

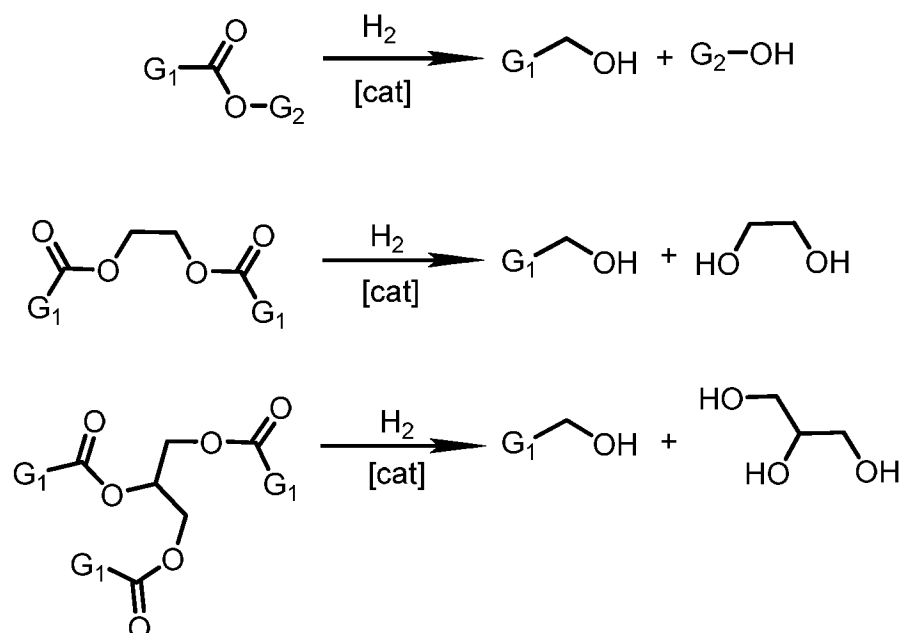
18. The process of claim 16, wherein R^9 comprises an amino group that can undergo dehydrogenation.

19. The process of claim 16, wherein R^9 is methyl.
20. The process of claim 16, wherein the substrate and product pair of the dehydrogenation reaction comprises:

Substrate	Product
alcohol	ester
alcohol	aldehyde
alcohol	ketone
diol	lactone
amine + alcohol	amide
amine + alcohol	substituted amine
amine + alcohol	imine
ammonia-borane	aminoboranes
ammonia-borane	borazine
amine	imine
amines	guanidine
alcohol + thiol	thioester
thiol	sulphoxide, or
alcohol + phosphine	acyl phosphine

21. A process for producing H_2 comprising dehydrogenation of a substrate by treating the substrate with a catalytic amount of the complex of any one of claims 8-13.
22. The process of claim 21, wherein the substrate comprises an alcohol, amine or thiol.
23. The process of claim 21, wherein the substrate is ammonia-borane.
24. The process of any one of claims 14-23, wherein the process does not require a hydrogen acceptor.
25. The process of any one of claims 14-24, which is a homogeneous process.
26. A process for hydrogenation of a substrate comprising treating the substrate with a catalytic amount of the complex of any one of claims 8-13 in the presence of molecular hydrogen.
27. The process of claim 26, wherein the substrate comprises at least one ester.

28. The process of claim 27, wherein the process proceeds in the presence of molecular hydrogen according to one of the following schemes



29. The process of claim 26, wherein the substrate and product pair of the hydrogenation reaction comprises:

Hydrogenation Substrate	Product
aldehyde	alcohol
ketone	alcohol
ester	alcohol
carboxylic acid	alcohol
ketene	alcohol
enol	alcohol, or
epoxide	alcohol
aldimine	amine
ketimine	amine
ketene-imine	amine
nitrile	amine
aziridine	amine
nitro	amine
diazo	amine
isocyanide	amine

Hydrogenation Substrate	Product
enamine	amine
lactone	diol
amide	amine + alcohol
aminoboranes	amine-borane
borazine	amine-borane
olefin	alkane
acetylene	alkane
allene	alkane

30. The process of any one of claims 24-29, which is a solvent-free process.
31. A process for producing ethyl acetate comprising treating ethanol with a catalytic amount of the complex of any one of claims 8-13.
32. The process of claim 31, which is a homogeneous process.
33. The process of claim 31 or 32, which does not require a hydrogen acceptor.