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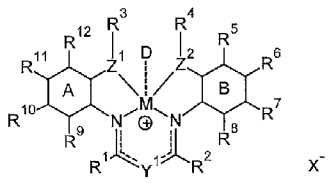
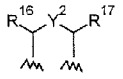
(54) Title: PROCESS



(I)



(AB)

(57) Abstract: The present invention relates to a process for the production of hydrogen comprising contacting at least one complex of formula (I), (I) wherein: X^- is an anion; M is a metal selected from Ru, Os, Fe, Co and Ni; D is optionally present and is one or more monodentate or multidentate donor ligands; Y^1 is selected from CR^{13}, B and N; Z^1 and Z^2 are each independently selected from =N, =P, NR^{14}, PR^{15}, O, S and Se; or Z^2 is a direct bond between carbocyclic ring B and substituent R^4; each of A and B is independently a saturated, unsaturated or partially unsaturated carbocyclic hydrocarbon ring; R^3 and R^4 are each independently selected from H, C_{1-6}-alkyl, aryl and C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support; or R^3 and R^4 together form the following moiety: (AB) Y^2 is a direct single bond or double bond, or is CR^{18}; R^1, R^2, R^{5-13} and R^{16-18} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, $NR^{19}R^{20}$ and a linker group optionally attached to a solid support; or two or more of said R^{1-13} and R^{16-18} groups are linked, together with the carbons to which they are attached, to form a saturated or unsaturated hydrocarbon group; R^{14}, R^{15}, R^{19} and R^{20} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support; with at least one substrate of formula (II), $R^{21}R^{22}NBHR^{23}R^{24}$, wherein R^{21} to R^{24} are each independently selected from H, C_{1-6}-alkyl, fluoro- substituted C_{1-6}-alkyl, C_{6-14}-aryl and C_{6-14}-aralkyl, or any two of R^{21}, R^{22}, R^{23} and R^{24} are linked to form a C_{3-10}-alkylene group or C_{3-10}-alkenylene group, which together with the nitrogen and/or boron atoms to which they are attached, forms a cyclic group; or a substrate comprising two, three or four substrates of formula (II) linked via one or more bridging groups so as to form a dimeric, trimeric or tetrameric species, and wherein the bridging group is selected from straight or branched C_{1-6}-alkylene optionally substituted by one or more fluoro groups, boron, C_{6-14}-aryl and C_{6-14}-aralkyl; or a substrate comprising two, three or four substrates of formula (II) which are joined so as to form a fused cyclic dimeric, trimeric or tetrameric species. Further aspects of the invention relate to a hydrogen generation system comprising a complex of formula (I), a substrate of formula (II) and a solvent, and to the use of complexes of formula (I) in fuel cells. Another aspect of the invention relates to novel complexes of formula (I).

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PROCESS

The present invention relates to a process for the production of dihydrogen. More specifically, the invention relates to a process for catalysing the release of dihydrogen from ammonia borane, and derivatives thereof, using a transition metal catalyst. The process of the invention has important applications in the field of hydrogen fuel cells.

BACKGROUND TO THE INVENTION

The combustion of hydrogen and oxygen is regarded as the cleanest possible source of energy, with water as the only product. Scientific agencies across the globe have clearly stated the need for the safe storage of hydrogen, which at high pressure is extremely explosive. In order to secure practical useable amounts of hydrogen, reinforced heavy steel walled pressurized gas tanks are generally used. In transportation applications, this leads to a significant waste of energy in carrying the extra weight required for the hydrogen cylinder. Moreover, the refilling of pressurized hydrogen represents a significant hazard.

One way of solving the problem of safe transportation is to use chemical hydrides as an alternative source of releasable hydrogen. Chemical hydrides can be packaged as non-pyrophoric, non-hazardous, solid, slurried or liquid fuels. Hydrogen may then be generated on demand from the chemical hydride under controlled conditions. Ideally, hydrogen storage materials have a high hydrogen content and a low molecular weight. One such example is ammonia borane, H_3N-BH_3, which has a very high hydrogen content by weight (19.2 %) and is attracting attention as a means of achieving efficient chemical hydrogen storage.

Although the cost of ammonia borane is still high compared to other hydrides, substantial research efforts are directed to finding new methods of synthesis. Numerous methods for obtaining large amounts of hydrogen from ammonia borane are documented in the art (Reviews: Chem. Soc. Rev. 2009, 38, 279-293; Chem. Rev. 2010, 110, 4079-4124). The formation of very stable B-O bonds is a major drawback of solvolysis methods, which makes the regeneration of spent fuel difficult. This problem is overcome with the use of catalysts in non-aqueous solutions under mild conditions.

More recently, Weller and Lloyd-Jones *et al* (J. Am. Chem. Soc., 2012, 134, 3598-3610) described the use of a rhodium-based catalyst, $[Rh(PCy_3)_2]^+$, for the dehydrocoupling of amino boranes. Williams *et al* (Chem Commun Camb, 2010 Jul 14;46(26):4815-7; Organometallics 2012, 30, 6705-6714; and US20120201744; University of Southern California) described the dehydrogenation of amino borane by Shvo's catalyst, a cyclopentadienone-ligated ruthenium complex. A second generation catalyst based on Shvo's catalyst is also disclosed. Schneider *et al* (Angew. Chem. Int. Ed. 2009, 48, 905-907) described ruthenium complexes with tridentate PNP (diphosphinoamine) ligands as bifunctional catalysts for the dehydrogenation of ammonia borane.

US 2009274613 (Hamilton *et al*) discloses the production of hydrogen from ammonia borane using a catalyst complex of the formula L_n-M-X, where M is a base metal such as Fe, Mn, Co, Ni and Cu, X is an anionic nitrogen- or phosphorus-based ligand or hydride, and L is a neutral ancillary ligand that is a neutral monodentate or polydentate ligand.

US 7,544,837 (Blacquiere *et al*) describes a method of dehydrogenating an amine-borane of formula $R^1H_2N\text{-}BH_2R^2$ using a base metal catalyst, to generate hydrogen and at least one of a $[R^1HN\text{-}BHR^2]_m$ oligomer and a $[R^1N\text{-}BR^2]_n$ oligomer. Base metal catalysts are defined as transition metals other than Pt, Pd, Rh, Os and Ru. The method has applications in the field of fuel cells.

The use of ligand stabilized homogenous catalysts containing Ru, Co, Ir, Ni and Pd to catalyse the release of hydrogen from ammonia borane is also described in WO 2008141439 (Kanata Chemical Technologies Inc.). Suitable ligands include phosphines, aminophosphines, heterocyclic ligands, diaminophosphines, diamines, thiophines and thioamines.

US 20080159949 (Mohajeri *et al*) discloses a method of generating hydrogen from an ammonia borane complex using catalysts including cobalt complexes, noble metal complexes and metallocenes. Examples of suitable noble metal catalysts include $NaRhCl_6$, chlorotris(triphenylphosphine) Rh (I), $(NH_4)_2RuCl_6K_2PtCl_6$, $(NH_4)_2PtCl_6Na_2PtCl_6$, H_2PtCl_6, $Fe(C_5H_5)_2$ and di-μ-chlorobis(p-cymene)chlororuthenium.

The method is suitable for use in polymer electrolyte membrane fuel cells (also known as proton exchange or PEMFCs).

JP2011-116681 (Hiroyuki *et al*) discloses an Fe based metal-boron complex as catalyst to dehydrogenate ammonia borane.

Over recent years, significant effort has been put into developing new hydrogen storage methods. However, all of the methods reported to date feature a number of potential drawbacks which potentially limit their commercial applications. The first is the high cost associated with the iridium or rhodium metal catalysts reported to date. The second problem is sensitivity to atmospheric oxygen, which at low levels significantly deactivates iridium and rhodium-based systems. Thus, it would be advantageous to develop a catalyst which shows a higher degree of tolerance to atmospheric oxygen.

Moreover, only few catalysts achieve high hydrogen release activity under mild conditions.

More importantly, the majority of homogenous metal-based dehydrogenation catalytic complexes developed to date tend to operate and produce high pressures even at the storage stage. This leads to potential safety hazards which necessitate the use of reaction containers that are able to withstand significantly higher pressures. Synthesis and further adaptation of the ligand system is difficult and requires multiple steps with costly separations.

Finally, reversibility through regeneration back to original ammonia borane is not feasible with many of the single site metal catalysts reported to date. Furthermore, these single site catalysts do not possess the ability to switch off at low hydrogen pressure, thereby creating potentially dangerous pressures, especially in situations where the cell is exposed to elevated temperatures.

Recent studies by the present applicant investigated the application of β-diketiminato arene-substituted Ru(II) complexes as bifunctional, i.e. dual-site, catalysts in the dehydrocoupling of amino boranes (Phillips *et al*, ACS Catal. 2012, 2, 2505-2511; and WO 2011151792; Nova UCD). Various structural analogues are also described. The

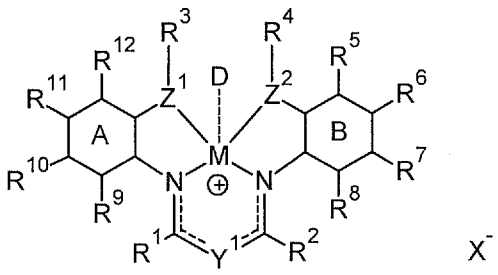
catalysts rapidly perform homolytic cleavage of hydrogen under mild conditions through bifunctional metal-ligand interaction. The β-diketiminato-ruthenium type complexes described by the authors offer several advantages, the most important being liberating H_2 from ammonia borane in a potentially reversible way.

The present invention seeks to provide alternative methods of generating hydrogen. Specifically, the invention seeks to provide a means for storing hydrogen that allows for the controlled and safe release of dihydrogen at a constant rate. In a preferred aspect, the invention seeks to provide catalysts suitable for the catalytic dihydrogen decoupling of ammonia boranes that exhibit improved turnover and/or enhanced reaction kinetics compared to catalysts previously described in the art. Moreover, the present catalyst offer improved long term stability to oxygen and moisture.

STATEMENT OF INVENTION

The present invention broadly relates to a process for the catalytic dihydrogen decoupling of ammonia borane and derivatives thereof.

More specifically, a first aspect of the invention relates to a process for the production of dihydrogen comprising contacting at least one complex of formula (I),



(I)

wherein:

X^- is an anion;

M is a metal selected from Ru, Os, Fe, Co and Ni;

D is optionally present and is one or more monodentate or multidentate donor ligands;

Y^1 is selected from CR^{13}, B and N;

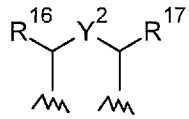
Z^1 and Z^2 are each independently selected from =N, =P, NR^{14}, PR^{15}, O, S and Se; or

Z^2 is a direct bond between carbocyclic ring B and substituent R^4;

each of A and B is independently a saturated, unsaturated or partially unsaturated carbocyclic hydrocarbon ring;

R^3 and R^4 are each independently selected from H, C_{1-6}-alkyl, aryl and C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support; or

R^3 and R^4 together form the following moiety:



Y^2 is a direct single bond or double bond, or is CR^{18};

R^1, R^2, R^{5-13} and R^{16-18} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, $NR^{19}R^{20}$ and a linker group optionally attached to a solid support;

or two or more of said R^{1-13} and R^{16-18} groups are linked, together with the carbons to which they are attached, to form a saturated or unsaturated hydrocarbon group;

R^{14}, R^{15}, R^{19} and R^{20} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support;

with at least one substrate of formula (II)

$$R^{21}R^{22}NH{-}BH{-}R^{23}R^{24}$$

(II)

wherein R^{21} to R^{24} are each independently selected from H, C_{1-6}-alkyl, fluoro-substituted C_{1-6}-alkyl, C_{6-14}-aryl and C_{6-14}-aralkyl, or any two of R^{21}, R^{22}, R^{23} and R^{24} are linked to form a C_{3-10}-alkylene group or C_{3-10}-alkenylene group, which together with the nitrogen and/or boron atoms to which they are attached, forms a cyclic group;

or a substrate comprising two, three or four substrates of formula (II) linked via one or more bridging groups so as to form a dimeric, trimeric or tetrameric species, and wherein the bridging group is selected from straight or branched C_{1-6}-alkylene optionally substituted by one or more fluoro groups; boron; C_{6-14}-aryl; and C_{6-14}-aralkyl;

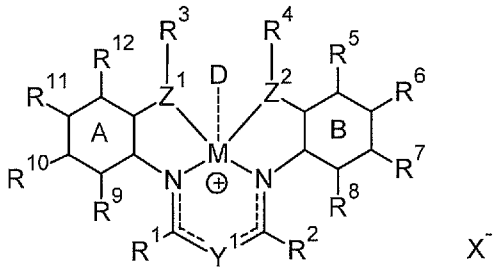
or a substrate comprising two, three or four substrates of formula (II) which are joined so as to form a fused cyclic dimeric, trimeric or tetrameric species.

Advantageously, the presently described process involves the use of a homogenous catalyst that activates gaseous dihydrogen. *Ab initio* calculations and experimental evidence have shown that a bifunctional mechanism is operative for the dehydrocoupling of ammonia borane. Thus, the unique dual site design of the β-diketiminato-metal complex offers the possibility for reversible H_2 coupling, thereby regenerating the original ammonia borane and eliminating the need for external removal and reloading of the energy storage medium.

The presently claimed catalyst system displays enhanced dehydrogenation kinetics compared to the previously described first generation systems described in WO 2011151792. The present catalysts can be synthesized in high yield from commercially available precursors and in the solid state under N_2 stored indefinitely. The catalyst-to-substrate ratio directly controls the rate of H_2 released. The catalysts are capable of extracting up to two equivalents of H_2 from the ammonia borane substrate.

A second aspect of the invention relates to a hydrogen generation system comprising:

(a) at least one complex of formula (I)



(I)

wherein:

X^- is an anion;

M is a metal selected from Ru, Os, Fe, Co and Ni;

D is optionally present and is one or more monodentate or multidentate donor ligands;

Y^1 is selected from CR^{13}, B and N;

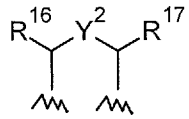
Z^1 and Z^2 are each independently selected from =N, =P, NR^{14}, PR^{15}, O, S and Se; or

Z^2 is a direct bond between carbocyclic ring B and substituent R^4;

each of A and B is independently a saturated, unsaturated or partially unsaturated carbocyclic hydrocarbon ring;

R^3 and R^4 are each independently selected from H, C_{1-6}-alkyl, aryl and C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support; or

R^3 and R^4 together form the following moiety:



Y^2 is a direct single bond or double bond, or is CR^{18};

R^1, R^2, R^{5-13} and R^{16-18} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, $NR^{19}R^{20}$ and a linker group optionally attached to a solid support;

or two or more of said R^{1-13} and R^{16-18} groups are linked, together with the carbons to which they are attached, to form a saturated or unsaturated hydrocarbon group;

R^{14}, R^{15}, R^{19} and R^{20} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support;

(b) at least one substrate of formula (II)

$$R^{21}R^{22}NH\text{-}BHR^{23}R^{24}$$

(II)

wherein R^{21} to R^{24} are each independently selected from H, C_{1-6}-alkyl, fluoro-substituted C_{1-6}-alkyl, C_{6-14}-aryl and C_{6-14}-aralkyl, or any two of R^{21}, R^{22}, R^{23} and R^{24} are linked to form a C_{3-10}-alkylene group or C_{3-10}-alkenylene group, which together with the nitrogen and/or boron atoms to which they are attached, forms a cyclic group;

or a substrate comprising two, three or four substrates of formula (II) linked via one or more bridging groups so as to form a dimeric, trimeric or tetrameric species, and wherein the bridging group is selected from straight or branched C_{1-6}-alkylene optionally substituted by one or more fluoro groups; boron; C_{6-14}-aryl; and C_{6-14}-aralkyl;

or a substrate comprising two, three or four substrates of formula (II) which are joined so as to form a fused cyclic dimeric, trimeric or tetrameric species; and

(c) optionally, a solvent.

A third aspect of the invention relates to the use of at least one complex of formula (I) as defined above in a fuel cell.

A fourth aspect of the invention relates to a fuel cell comprising at least one complex of formula (I) as defined above.

A fifth aspect of the invention relates to a method of thermolytically dehydrogenating a substrate of formula (II) as described above, said method comprising contacting at least one substrate of formula (II) with a complex of formula (I) in the presence of a solvent.

A sixth aspect of the invention relates to the use of at least one complex of formula (I) as defined above in a method of thermolytically dehydrogenating a substrate of formula (II) as described above.

A seventh aspect of the invention relates to the use of at least one complex of formula (I) as defined above in a method of producing hydrogen.

An eighth aspect of the invention relates to complexes of formula (I).

A ninth aspect of the invention relates to a method of using a hydrogen generation system as defined above which comprises modulating the hydrogen pressure in said system so as to modulate activity of the at least one complex of formula (I).

DETAILED DESCRIPTION

As used herein, the term "C_{1-n}alkyl" means straight or branched chain, saturated alkyl groups 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 group. In one preferred embodiment, the C_{1-n}alkyl group is a C_{1-20}-alkyl group, more preferably a C_{1-6}-alkyl group, even more preferably, a C_{1-3}-alkyl group.

As used herein, the term "C_{1-n}-haloalkyl" refers to a C_{1-n}-alkyl group as defined above in which one or more hydrogens are replaced with a halogen atom selected from Br, F, Cl and I. Preferably, the C_{1-n}-haloalkyl group is a C_{1-20}-haloalkyl group, more preferably a C_{1-10}-haloalkyl group, even more preferably, a C_{1-6}-haloalkyl group. In one particularly preferred embodiment, the C_{1-n}-haloalkyl group is a C_{1-n}-fluoroalkyl group, more preferably, a C_{1-20}-fluoroalkyl group, even more preferably a C_{1-10}-fluoroalkyl group, even more preferably still, a C_{1-6}-fluoroalkyl group. CF_3 is a particularly preferred C_{1-6}-fluoroalkyl group.

As used herein, the term "C_{6-n}aryl" means a monocyclic, bicyclic or tricyclic carbocyclic ring system containing from 6 to n carbon atoms and at least one aromatic ring and includes, depending on the identity of n, phenyl, naphthyl, anthracenyl, 1,2-dihydronaphthyl, 1,2,3,4-tetrahydronaphthyl, fluorenyl, indanyl, indenyl and the like, where the variable n is an integer representing the largest number of carbon atoms in the aryl group. In one preferred embodiment, the C_{6-n}aryl group is a C_{6-14}-aryl group, more preferably, a C_{6-10}-aryl group, even more preferably, a phenyl group.

As used herein, the term "aralkyl" means a conjunction of C_{1-n}alkyl or C_{1-n}-haloalkyl and C_{6-n}aryl as defined above. Preferred aralkyl groups include benzyl.

As used herein, the term "carbocyclic ring" means a carbon-containing ring system, that includes monocycles, fused bicyclic and polycyclic rings, bridged rings and metallocenes. Where specified, one or more carbons in the rings may be substituted or replaced with heteroatoms. Preferably, the carbocyclic group is cyclohexyl.

In one highly preferred embodiment, each of A and B is independently an unsaturated carbocyclic ring, more preferably a phenyl ring. Carbocyclic ring A is substituted by groups R^9-R^{12} as defined above, whereas carbocyclic ring B is substituted by groups R^5-R^8 as defined above.

As used herein, the term "fluoro-substituted" means that one or more, including all, of the hydrogens in the group have been 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.

A first aspect of the invention relates to a process for the production of hydrogen comprising contacting at least one complex of formula (I), with at least one substrate of formula (II) as defined above. Preferably, the process is carried out in the presence of a suitable solvent.

The invention consists of a catalyzed chemical process for the controlled and safe release of hydrogen at constant rate from the substrate ammonia borane or related organic N,B-substituted derivatives. The overall purpose of the process is to provide a constant flow rate of high purity hydrogen for use in fuel cells or combustion engines, which in combination with atmospheric oxygen emit only water. No external heating, light or electricity is required to initiate the catalytic dehydrogenation process. Hydrogen has been shown to carry an extremely high energy to mass ratio of 120 MJ kg^{-1} as compared to conventional gasoline products (44 MJ kg^{-1}).

The present applicant has synthesized a series of different derivatives of the catalytic complex. A number of these have been tested in dehydrogenation reactions under different conditions (variation of substrate, solvent, concentration, temperature) and in direct comparison to catalysts of the first generation (see, for example, WO 2011151792). The release of over two equivalents of H_2 from ammonia borane was achieved.

The applicant's previous application (WO 2011151792) described the unique dual site design of the β-diketiminato-ruthenium complex, which offers the possibility for reversible H_2 coupling, thereby regenerating the original ammonia borane and eliminating the need for external removal and reloading the energy storage medium.

The presently claimed invention provides a significantly improved dual site catalyst system. The unique tetra-coordinating anionic diketiminato ligand leads to an immediate loss of the supporting ligand in solution, creating a large free reactive site and consequently enhanced reaction kinetics. Moreover the catalytic activity of the β-diketiminato-ruthenium complex can be modified through simple changes in the ligand

design. Anchoring of the catalyst to solid support is also possible, thereby facilitating easy separation of the spent materials.

Substrate of formula (II)

The process of the invention uses a substrate of formula (II), $R^{21}R^{22}NH\text{-}BHR^{23}R^{24}$, as described above.

Preferably, R^{21}, R^{22}, R^{23} and R^{24} are each independently selected from H, C_{1-10}-alkyl, fluoro-substituted-C_{1-10}-alkyl, C_{6-10}-aryl and C_{6-10}-aralkyl, or any two of R^{21}, R^{22}, R^{23} and R^{24} are linked to form a C_{2-6}-alkylene group, which together with the nitrogen and/or boron atoms to which they are attached, forms a cyclic group.

More preferably, R^{21}, R^{22}, R^{23} and R^{24} are each independently selected from H, C_{1-6}-alkyl, fluoro-substituted-C_{1-6}-alkyl, C_6-aryl and C_{6-10}-aralkyl, or any two of R^{21}, R^{22}, R^{23} and R^{24} are linked to form a C_{2-6}-alkylene group, which together with the nitrogen and/or boron atoms to which they are attached, forms a cyclic group.

In one preferred embodiment, R^{23} and R^{24} are both H.

In one preferred embodiment, R^{23} and R^{24} are both H, and R^{21} and R^{22} are each independently selected from H, C_{1-10}-alkyl, fluoro-substituted-C_{1-10}-alkyl, C_{6-10}-aryl and C_{6-10}-aralkyl, or R^{21} and R^{22} are linked to form a C_{2-6}-alkylene group, which together with the nitrogen atom to which they are attached, forms a cyclic group.

More preferably, R^{23} and R^{24} are both H and R^{21} and R^{22} are each independently selected from H, C_{1-10}-alkyl, fluoro-substituted-C_{1-10}-alkyl and C_{6-10}-aryl.

In one preferred embodiment of the invention, R^{21}, R^{22}, R^{23} and R^{24} are each independently selected from H and C_{1-20}-alkyl.

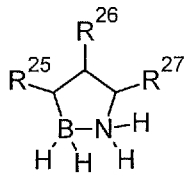
In one highly preferred embodiment, R^{23} and R^{24} are both H, one of R^{21} and R^{22} is H and the other is selected from H, C_{1-10}-alkyl, C_{1-10}-fluoroalkyl, C_{6-10}-aryl and C_{6-10}-aralkyl.

More preferably, one of R^{21} and R^{22} is H and the other is selected from H, methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl, tert-butyl, CF_3, fluorinated alkyl, sec-butyl, phenyl and benzyl.

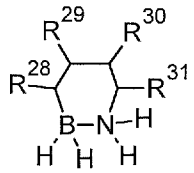
In another highly preferred embodiment, R^{23} and R^{24} are both H, and R^{21} and R^{22} are each independently selected from H, methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl, tert-butyl, sec-butyl, phenyl and benzyl, CF_3, or R^{21} and R^{22} are linked to form a C_{2-6}-alkylene group, which together with the nitrogen atom to which they are attached, form a cyclic group. Preferably, where R^{21} and R^{22} are linked to form a C_{2-6}-alkylene group, the C_{2-6}-alkylene group is a C_4-alkylene group.

In one preferred embodiment, two of R^{21}, R^{22}, R^{23} and R^{24} are linked to form a C_{2-10}-alkylene group, which together with the nitrogen and/or boron atoms to which they are attached, forms a cyclic group.

By way of example, in one particularly preferred embodiment, the substrate of formula II is selected from the following:



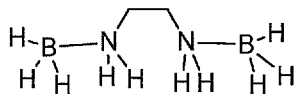
(III)



(IV)

wherein each of R^{25} to R^{31} is independently selected from alkyl and H. Compounds of formulas (III) and (IV) are described in Wei Luo, Lev N. Zakharov, and Shih-Yuan Liu, J. Am. Chem. Soc. 2011, 133, 13006–13009, and Wei Luo, Patrick G. Campbell, Lev N. Zakharov, and Shih-Yuan Liu, J. Am. Chem. Soc. 2011, 133, 19326–19329.

In another preferred embodiment, the substrate of formula II is of formula:



Compounds of this type are described in Neiner, D.; Karkamkar, A,; Bowden, M.; Choi, J. Y.; Luedtke, A.; Holladay, J.; Fisher, A.; Szymczakc, N.; Autrey, T.: Energy Environ. Sci., 2011, 4, 4187.

In one preferred embodiment, the substrate of formula (II) is selected from ammonia borane, methylamine borane, dimethylamine borane, di-isopropylamine borane, isopropylamine borane, tert-butylamine borane, isobutylamine borane, phenylamine borane and pyrrolidine borane.

In one highly preferred embodiment, the substrate of formula (II) is dimethylamine borane.

In another highly preferred embodiment, the substrate of formula (II) is ammonia borane, H_3B-NH_3, i.e. R^{21}, R^{22}, R^{23} and R^{24} are all H. Ammonia borane is a non-combustible, industrially inexpensive, low molecular weight solid substrate that carries multiple molecular equivalents of hydrogen. Ammonia borane has a high hydrogen carrying capacity of 19.6% per weight and is not flammable. This is consistent with the objectives set forth by the US Department of Energy of 5.5 wt% in vehicles by 2015. Using a small amount (typically 0.5 to 1% mol) of a molecular catalyst (consisting of a metal and supporting organic ligands), decouples multiple equivalents of gaseous hydrogen from ammonia borane at a sustained rate at room temperature, or at elevated temperatures between 42 and 74°C.

Complex of formula (I)

The process of the invention utilises a complex of formula (I), as defined above, as a catalyst. The catalyst is a bifunctional dual site complex consisting of a transition metal and a ligand that is robust and stable over long periods of storage and reaction time.

In contrast to the first generation catalysts described in our earlier application (WO 201151792), which are η^6-arene κ^2-β-diketiminato ruthenium complexes, the presently claimed catalysts are tethered κ^3-substitued-β-diketiminato or κ^4-substituted-β-diketiminato ruthenium complexes. Advantageously, the presently claimed catalyst structures afford faster dehydrogenation kinetics compared to the first generation catalysts. As the rate of H_2 released also depends on the catalyst to substrate ratio, the additional benefit of this second catalyst generation can be, depending on the

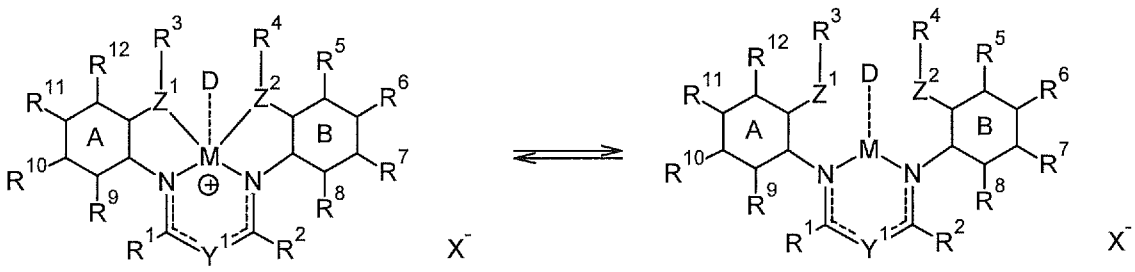
application, twofold: (i) to achieve a higher H_2 release rate, and/or (ii) to lower the amount of catalyst used (and consequently the cost of the system).

Advantageously, the presently claimed catalysts show a high degree of tolerance. Every catalyst is restricted by its turnover frequency, which determines the reaction kinetics and, by the amount of catalyst needed to achieve a certain rate, also the cost of the system. Any increase in the turnover number therefore represents a valuable contribution to the art. Compared to the first generation of catalysts described in WO 2011151792, the second generation of catalysts presented here excels in an increased turnover frequency.

It is understood that generally at some point, the donor ligand D dissociates in solution to form the active catalytic species, although at some point re-association cannot be ruled out. Some of the compounds are isolated after synthesis as a mixture of the complex with the donor ligand D and the complex where D has been lost. These mixtures can be used without further separation in the dehydrogenation experiments.

Further, it has to be noted that the coordination between M and Z^1 and/or M and Z^2 is not always clearly defined. The solid bond drawn in the structures between M and Z^1 or M and Z^2 therefore cannot be understood as excluding non-coordination for both Z^1 and Z^2 (as shown in the equilibrium between coordination and non-coordination below) or for any of Z^1 and Z^2 independently. The skilled person will be familiar with this nomenclature and structural representation of coordination sites.

For example, in one preferred embodiment, where the donor ligand D is η^6-arene, Z^1 and Z^2 do not coordinate to M. However, in another preferred embodiment, where donor ligand D is absent, Z^1 and Z^2 do coordinate to M.



In one preferred embodiment of the invention, X^- is selected from OTf^-, BF_4^-, PF_6^-, BPh_4^- or $BArF^-$ ($B((3,5\text{-}CF_3)_2C_6H_3)_4^-$), more preferably, OTf^-. As used herein, X^- does not imply a specific bond type to the metal M. X^- represents any bond type between the limits of a non-coordinated anion and a coordinated ligand with formally negative charge. In other words, X^- may or may not coordinate - weakly or strongly - with metal M.

In one preferred embodiment of the invention, M is selected from Ru, Ni and Co. More preferably, M is Ru.

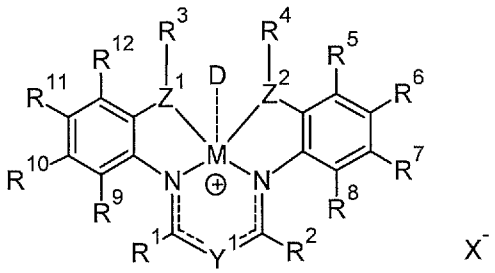
In one preferred embodiment of the invention, R^5-R^{12} are each independently selected from H, methyl, CF_3 and isopropyl.

In one preferred embodiment of the invention, R_1 and R_2 are both independently $C_{1\text{-}6}$-alkyl, more preferably, methyl.

In one preferred embodiment of the invention, Y^1 is CR^{13}, more preferably CH.

In formula (I), Z^1 and Z^2 are each independently selected from =N (double bonded to R^3 or R^4 respectively, or double bonded to ring A or ring B respectively), =P (double bonded to R^3 or R^4 respectively, or double bonded to ring A or ring B respectively), NR^{14}, PR^{15}, O, S and Se,

In one preferred embodiment of the invention, A and B are both phenyl groups, i.e. the compound is of formula (V):



(V)

wherein R^1-R^{12}, D, M, Y^1, Z^1, Z^2 and X^- are as defined above.

In one preferred embodiment of the invention, Z^1R^3 and Z^2R^4 are each independently S-C_{1-6}-alkyl, more preferably Z^1R^3 and Z^2R^4 are each independently selected from SCH_3 and SCH_2CH_3.

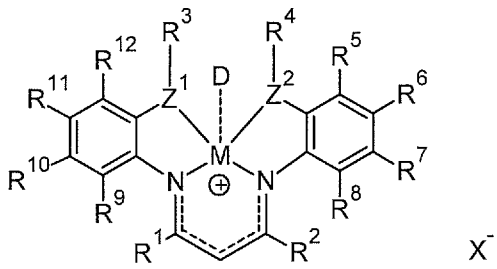
In one preferred embodiment of the invention, Z^1R^3 is S-C_{1-6}-alkyl, Z^2 is a direct bond and R^4 to R^8 are independently C_{1-6}-alkyl, more preferably Z^1R^3 is selected from SCH_3 and SCH_2CH_3 and Z^2 is a direct bond, and R^4 and R^8 are methyl.

In one preferred embodiment of the invention, Z^1 and Z^2 are each independently selected from S and NR^{14}.

In one preferred embodiment of the invention, Z^1 is selected from S and NR^{14}, and Z^2 is a direct bond.

In one preferred embodiment of the invention, Z^2R^1 and Z^1R^2 together form the following moiety:

In one preferred embodiment, the complex is of formula (Va)



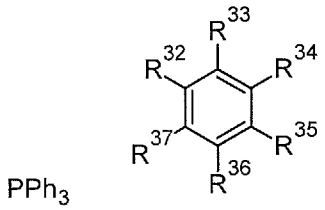
(Va)

wherein:

X^- is an anion selected from Cl^-, Br^-, PF_6^-, TfO^-;

M is selected from Ru and Ni;

D is optional and is selected from (VI) and (VII),



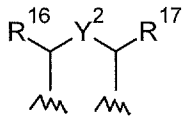
PPh_3

(VI) (VII)

Z^1 and Z^2 are each independently selected from NR^{14}, PR^{15}, O and S; or Z^2 is a direct bond to R^4;

R^3 and R^4 are each independently selected from H, C_{1-6}-alkyl, aryl and C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support; or

R^3 and R^4 together form the following moiety:



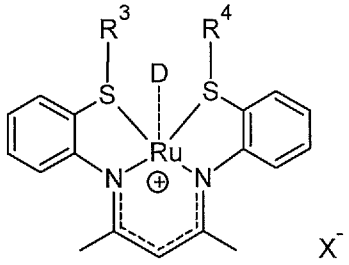
Y^2 is a direct single bond or double bond, or is CR^{18};

R^1, R^2, R^{5-13} and R^{16-18} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, $NR^{19}R^{20}$ and a linker group optionally attached to a solid support;

or two or more of said R^{1-13} and R^{16-18} groups are linked, together with the carbons to which they are attached, to form a cyclic saturated or unsaturated hydrocarbon group;

R^{14}, R^{15}, R^{19}, R^{20} and R^{32-37} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support.

In one preferred embodiment of the invention, the compound of formula (I) is a compound of formula (VIII):



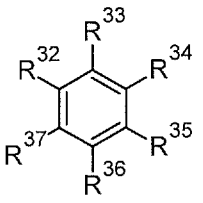
(VIII)

wherein R_3, R_4, D and X^- are as defined as above.

In one particularly preferred embodiment, the complex of formula (I) is of formula (VIII) as defined above, wherein:

X^- is an anion selected from Cl^- and TfO^-;

D is optional and is selected from (VI) and (VII),



PPh_3

(VI)

(VII)

R^3 and R^4 are each independently selected from H, C_{1-6}-alkyl, aryl and C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support.

In one preferred embodiment of the invention,

(i) D is η^6-C_6H_6, and X^- is Cl^-;

(ii) D is η^6-C_6H_6, and X^- is OTf^-;

(iii) D is absent, and X^- is Cl^-;

(iv) D is absent, and X^- is OTf^-;

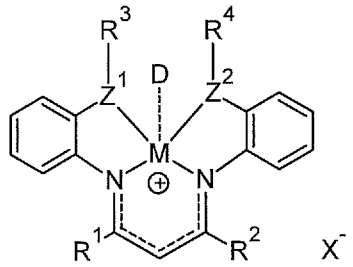
(v) D is PPh_3, and X^- is Cl^-;

(vi) D is PPh_3, and X^- is OTf^-; or

(vii) D is absent, and X^- is Br^-.

Where D is present, the first step in the reaction is the loss of this ligand to form a precursor. The precursor so formed is then capable of interacting with the substrate of formula (II).

In one particularly preferred embodiment of the invention, the compound of formula (I) is a compound of formulas (IXa-IXb) selected from the following:



(IXa)

Compound 6a: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Cl^-

Compound 6b: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; X^- = Cl^-

Compound 6c: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; X^- = Cl^-

Compound 6d: M = Ru; D = η^6-C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; X^- = Cl^-

Compound 6e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

Compound 6f: M = Ru; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

Compound 6g: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; X^- = OTf^-

Compound 6h: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; X^- = OTf^-

Compound 6i: M = Ru; D = η^6-C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; X^- = OTf^-

Compound 6j: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Cl^-

Compound 6k: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

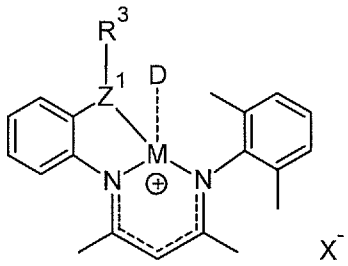
Compound 6l: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Br^-

Compound 6m: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = PF_6^-

Compound 6n: M = Ni; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^3 and R^4 together = CH_2CH_2; X^- = PF_6^-

Compound 6q: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-2} = H; R^{3-4} = CH_3; X^- = OTf^-

Compound 6r: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-2} = H; R^{3-4} = CH_3; X^- = Cl^-

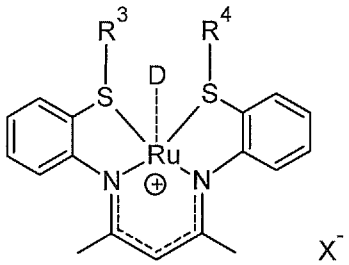


(IXb)

Compound 6o: M = Ru; D = η^6-C_6H_6; Z^1 = S; R^3 = CH_3; X^- = Cl^-

Compound 6p: M = Ru; D = η^6-C_6H_6; Z^1 = S; R^3 = CH_3; X^- = OTf^-

In one highly preferred embodiment of the invention, the complex of formula (I) is a compound of formula (X) selected from the following:



(X)

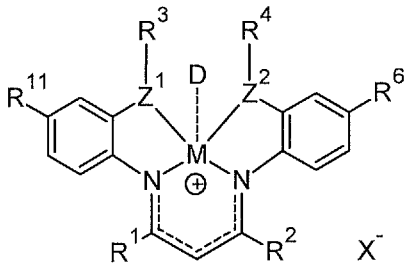
Compound 6e: D = η^6-C_6H_6; R^{3-4} = CH_3; X^- = OTf^-

Compound 6g: D = η^6-C_6H_6; R^{3-4} = CH_2CH_3; X^- = OTf^-

Compound 6j: D = PPh_3; R^{3-4} = CH_3; X^- = Cl^-

Compound 6k: D = PPh_3; R^{3-4} = CH_3; X^- = OTf^-

In another preferred embodiment, the compound of formula (I) is selected from the following:



(IXa)

Compound 6a: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6b: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6c: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6d: M = Ru; D = η^6-C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6f: M = Ru; D = none; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6g: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6h: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6i: M = Ru; D = η^6-C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6j: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6k: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6l: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = Br^-

Compound 6m: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = PF_6^-

Compound 6n: M = Ni; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^3 and R^4 together = CH_2CH_2; $R^{6,11}$ = H; X^- = PF_6^-

Compound 6q: M = Ru; D = PPh_3; Z^{1-2} = S; $R^{1-2,6,11}$ = H; R^{3-4} = CH_3; X^- = ^-OTf

Compound 6r: M = Ru; D = PPh_3; Z^{1-2} = S; $R^{1-2,6,11}$ = H; R^{3-4} = CH_3; X^- = Cl^-

Compound 11a: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; $R^{1-4,6,11}$ = CH_3; X^- = ^-OTf

Compound 11b: M = Ru; D = none; Z^{1-2} = S; $R^{1-4,6,11}$ = CH_3; X^- = ^-OTf

Compound 11c: M = Ru; D = η^6-(*p*-cymene); Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 11d: M = Ru; D = η^6-[$C_6(CH_3)_6$]; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

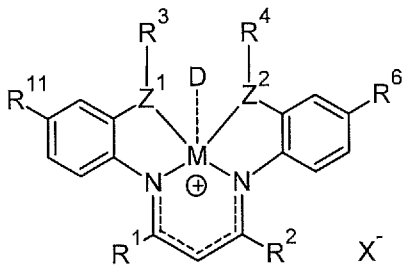
Compound 11e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = [(3,5-$(CF_3)_2C_6H_3)_4B]^-$

Compound 11f: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = SbF_6^-

Compound 11g: M = Os; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 11h: M = Os; D = none; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

In another preferred embodiment, the compound of formula (I) is selected from the following:



(IXa)

Compound 6e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6f: M = Ru; D = none; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6g: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6h: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6j: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6k: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 11a: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; $R^{1-4,6,11}$ = CH_3; X^- = ^-OTf

Compound 11b: M = Ru; D = none; Z^{1-2} = S; $R^{1-4,6,11}$ = CH_3; X^- = ^-OTf

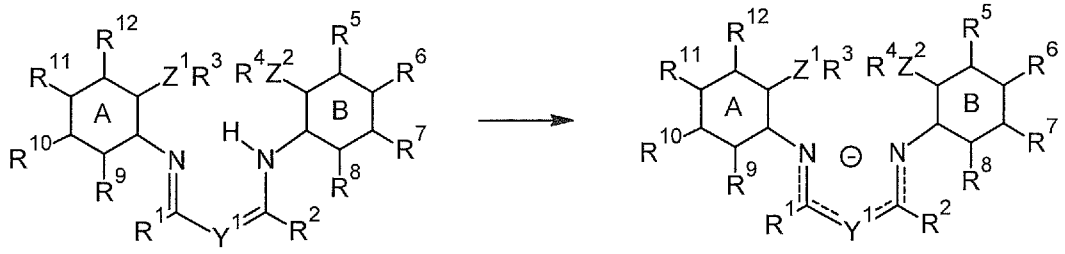
Compound 11c: M = Ru; D = η^6-(*p*-cymene); Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 11d: M = Ru; D = η^6-[$C_6(CH_3)_6$]; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 11e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = [(3,5-$(CF_3)_2C_6H_3)_4B]^-$

Compound 11f: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = SbF_6^-

As used herein, the complex of formula (I) is derived from a precursor that is a β-diketiminate-type ligand. Deprotonation of the structure shown on the left below (a β-diketimine type ligand) gives rise to a β-diketiminate-type ligand as shown on the right below, that is conventionally represented with the dashed lines showing a delocalisation of the negative charge. The negative charge may of course be further delocalised over the molecule, depending on the nature of the A and B rings.



β-diketimine type ligand **β-diketiminate-type ligand**

The β-diketiminate-type ligand is capable of forming a complex with Ru(II), Os(II) or Fe(II), for example, an η^6-arene β-diketiminato-ruthenium complex, an η^6-arene β-diketiminato-osmium complex or an η^6-arene β-diketiminato-iron complex. Throughout the specification, the coordination between the metal M and the donor ligand D (e.g., η^6-arene) is represented as a dashed line.

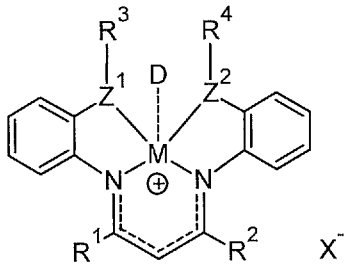
In one preferred embodiment, the complex of formula (I) is anchored to a solid support, for example, a polymer, thereby facilitating easy separation of the spent materials. Suitable solid supports will be familiar to one of ordinary skill in the art. Likewise, suitable linker groups for attaching the complex of formula (I) to the solid support will also be familiar to the skilled artisan.

The post-grafting of the catalyst to an insoluble solid surface is preferably achieved via attachment through one or more of the groups $R^1 - R^{20}$, i.e. one or more of the groups $R^1 - R^{20}$ is a linker group optionally attached to a solid support.

Preferably, the insoluble solid surface is mesoporous silica, e.g. MCM-41 containing hexagonal channels.
Preferably, the complex of formula (I) is anchored to the solid surface via a linear silanol alkyl tether.

The complex of formula (I) may be prepared and isolated prior to use in the process of the invention, or may be generated *in situ*.

Another aspect of the invention relates to specific complexes of formula (VII) selected from the following:



(IXa)

Compound 6a: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Cl^-

Compound 6b: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; X^- = Cl^-

Compound 6c: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; X^- = Cl^-

Compound 6d: M = Ru; D = η^6-C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; X^- = Cl^-

Compound 6e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

Compound 6f: M = Ru; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

Compound 6g: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; X^- = OTf^-

Compound 6h: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; X^- = OTf^-

Compound 6i: M = Ru; D = η^6-C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; X^- = OTf^-

Compound 6j: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Cl^-

Compound 6k: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

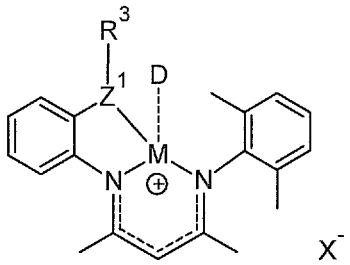
Compound 6l: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Br^-

Compound 6m: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = PF_6^-

Compound 6n: M = Ni; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^3 and R^4 together = CH_2CH_2; X^- = PF_6^-

Compound 6q: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-2} = H; R^{3-4} = CH_3; X^- = OTf^-

Compound 6r: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-2} = H; R^{3-4} = CH_3; X^- = Cl^-



(IXb)

Compound 6o: M = Ru; D = η^6-C_6H_6; Z^1 = S; R^3 = CH_3; X^- = Cl^-

Compound 6p: M = Ru; D = η^6-C_6H_6; Z^1 = S; R^3 = CH_3; X^- = OTf^-

Another preferred embodiment of the invention relates to a complex selected from 6a-6r and 11a to 11h as defined above. More preferably, the complex is selected from 6e-6h, 6j, 6k and 11a-f.

Process

The process of the reaction is typically carried out using a suitable solvent system. Preferably, the substrate of formula (II) is dissolved or slurried in a polar, non-protic solvent. Non-limiting examples of such solvents include toluene, chlorinated and fluorinated solvents such as methylene chloride and 1,2-dichlorobenzene, and ethereal solvents such as tetrahydrofuran (THF), 1,2-dimethoxyethane, diglyme and polyethylene glycol dimethyl ether. Such solvents may be used either individually or in combination with each other. Particularly preferred solvents include THF, 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, 1-butyl-3-methylimidazolium trifluoromethanesulfonate, 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-butyl-3-methylimidazolium bromide (BmimBr). Particularly preferred fluorinated solvents include α,α,α-trifluorotoluene.

In one highly preferred embodiment, the solvent is selected from THF, 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$), 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-butyl-3-methylimidazolium bromide (BmimBr).

Preferably, the process of the invention uses a non-volatile solvent, so that only dihydrogen is liberated during the reaction.

Preferably, the process of the invention takes place in a homogeneous mixture, i.e. preferably the complex of formula (I) is essentially soluble in the reaction solvent(s) and remains essentially in solution through the reaction process with minimal amounts of precipitation.

In another preferred embodiment, the process takes place without additional solvent. In that case, the substrate (II) is either liquid at the reaction temperature or in an mixture with the catalyst (I) or in a mixture of different substrates according to formula (II) due to melting point reduction in mixtures.

In one preferred embodiment, the solvent is a mixture of THF and dimethoxyethane. Preferably, the ratio of THF and dimethoxyethane is from about 4:1 to about 3:1.

Preferably, the complex of formula (I) is dissolved or slurried in solution with the same solvent as that used to dissolve or slurry the substrate of formula (II).

The catalyst to substrate ratio directly controls the rate of hydrogen released.

Preferably, the process of the invention is carried out at close to atmospheric pressure.

Advantageously, the process can be carried out without the need for an external heat source. Preferably, the process of the invention is carried out at a temperature of at least 0°C.

In one preferred embodiment, the process is carried out at room temperature (approximately 25°C).

In another preferred embodiment, the process is carried out at a temperature of from about 20°C to about 50°C, preferably from about 25°C to about 45°C, more preferably from about 30°C to about 45°C, more preferably still from about 35°C to about 45°C, even more preferably from about 40°C to about 45°C.

In another preferred embodiment, the process is carried out at a temperature of from about 50°C to about 80°C, preferably from about 60°C to about 80°C, more preferably from about 65°C to about 80°C, more preferably still from about 65°C to about 75°C, even more preferably from about 70°C to about 75°C.

The hydrogen that is generated in the process of the invention may be optionally captured using any known means. The reaction may be performed in air, but may also be performed in an inert atmosphere, for example, under argon or neon, or under hydrogen.

Preferably, the process of the invention is carried out in the absence of oxygen.

Preferably, the process of the invention is carried out in an inert atmosphere.

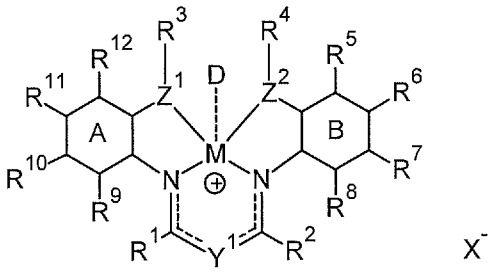
Surprisingly, the process of the invention can also be carried out in the presence of oxygen and/or water in the atmosphere. Thus, in one preferred embodiment, the process of the invention is carried out in the presence of oxygen. In another preferred embodiment, the process of the invention is carried out in the presence of oxygen and atmospheric water.

Hydrogen Generation System

There are expected to be many applications for the process of the present disclosure. In one embodiment, the process of the invention is used to generate hydrogen, which is supplied to a hydrogen fuel cell, such as a PEMFC. Hydrogen generators may include a first compartment holding a catalyst-comprising solution and a second compartment holding the one or more substrates of formula (II) as defined above.

A further aspect of the invention therefore relates to a hydrogen generation system comprising:

(a) at least one complex of formula (I)



(I)

wherein:

X^- is an anion;

M is a metal selected from Ru, Os, Fe, Co and Ni;

D is optionally present and is one or more monodentate or multidentate donor ligands;

Y^1 is selected from CR^{13}, B and N;

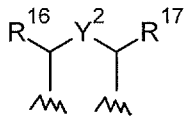
Z^1 and Z^2 are each independently selected from =N, =P, NR^{14}, PR^{15}, O, S and Se; or

Z^2 is a direct bond between carbocyclic ring B and substituent R^4;

each of A and B is independently a saturated, unsaturated or partially unsaturated carbocyclic hydrocarbon ring;

R^3 and R^4 are each independently selected from H, C_{1-6}-alkyl, aryl and C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support; or

R^3 and R^4 together form the following moiety:



Y^2 is a direct single bond or double bond, or is CR^{18};

R^1, R^2, R^{5-13} and R^{16-18} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, $NR^{19}R^{20}$ and a linker group optionally attached to a solid support;

or two or more of said R^{1-13} and R^{16-18} groups are linked, together with the carbons to which they are attached, to form a saturated or unsaturated hydrocarbon group;

R^{14}, R^{15}, R^{19} and R^{20} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support;

(b) at least one substrate of formula (II)

$R^{21}R^{22}NH\text{-}BHR^{23}R^{24}$

(II)

wherein R^{21} to R^{24} are each independently selected from H, C_{1-6}-alkyl, fluoro-substituted C_{1-6}-alkyl, C_{6-14}-aryl and C_{6-14}-aralkyl, or any two of R^{21}, R^{22}, R^{23} and R^{24} are linked to form a C_{3-10}-alkylene group or C_{3-10}-alkenylene group, which together with the nitrogen and/or boron atoms to which they are attached, forms a cyclic group;

or a substrate comprising two, three or four substrates of formula (II) linked via one or more bridging groups so as to form a dimeric, trimeric or tetrameric species, and wherein the bridging group is selected from straight or branched C_{1-6}-alkylene optionally substituted by one or more fluoro groups; boron; C_{6-14}-aryl; and C_{6-14}-aralkyl;

or a substrate comprising two, three or four substrates of formula (II) which are joined so as to form a fused cyclic dimeric, trimeric or tetrameric species; and

(c) optionally, a solvent.

In one preferred embodiment of the invention, the hydrogen generation system comprises a first compartment comprising the at least one complex of formula (I), a second compartment comprising the at least one substrate of formula (II), wherein the first or second compartment further comprises a solvent and/or a means for combining the contents of the first compartment with the contents of the second compartment such that when the contents are combined, hydrogen is generated.

More preferably, the hydrogen generation system further comprises at least one flow controller to control a flow rate of the at least one complex of formula (I) or the at least one substrate of formula (II).

Preferably, control electronics are coupled to substrate mass flow controllers and hydrogen mass flow controllers. Mass flow controllers control the flow of the substrate solution, which enters the first compartment to achieve a desired hydrogen flow

generated by the hydrogen generator. The catalyst contained in the first compartment may be tethered to a surface by a linker.

In one preferred embodiment, the at least one substrate of formula (II) is stored in a separated compartment as a solid, a liquid or as a solution in a solvent. In operation, as soon as the hydrogen generator is turned on, control electronics send a signal to a mass flow controller (or a flow controller) to allow a predetermined flow rate of the at least one substrate of formula (II) in a solvent (or in its liquid form) in a second compartment to flow into the first compartment which holds the complex of formula (I). As a result, hydrogen gas is generated. The reaction by-products are captured and remain in the first compartment. In alternate embodiments the complex of formula (I) in the solvent can be provided in the second compartment and be pumped into the first compartment holding the substrate of formula (II).

The hydrogen generation system is preferably in the form of a self-contained reaction vessel that is attached via a vent to any application requiring a source of hydrogen gas, for example, a chemical reaction, a fuel cell, or the like. Suitable fuel cells will be familiar to one skilled in the art and include any fuel cells that can use hydrogen as a fuel source, for example, internal combustion engines (ICE), solid oxide fuel cells (SOFC), phosphoric acid fuel cells (PAFC), alkaline fuel cells (AFC) and molten carbonate fuel cells (MCFC).

In one particularly preferred embodiment of the invention, the hydrogen generation system is connected to a proton exchange membrane fuel cell (PEMFC). More preferably, a coupling connector delivers hydrogen generated by hydrogen generator to the anode of a PEMFC.

The hydrogen generators disclosed herein are capable of delivering PEMFC grade hydrogen at low reaction temperatures, safely and reliably. Such hydrogen PEM fuel cells are optimal for applications where batteries and internal combustion engines do not deliver cost-effective and convenient power generation solutions. Advantageously, the hydrogen generators disclosed herein provide a constant source of power in a compact size that does not require electrical recharging.

Another aspect of the invention relates to the use of at least one complex of formula (I) as defined above in a fuel cell.

Another aspect of the invention relates to a fuel cell comprising at least one complex of formula (I) as defined above. Preferably, the fuel cell further comprises a substrate of formula (II) as defined above, and optionally a suitable solvent.

Another aspect of the invention relates to a method of thermolytically dehydrogenating a substrate of formula (II) as described above, said method comprising contacting at least one substrate of formula (II) with a complex of formula (I) in the presence of a solvent.

Another aspect of the invention relates to the use of at least one complex of formula (I) as defined above in a method of thermolytically dehydrogenating a substrate of formula (II) as described above.

Another aspect of the invention relates to the use of at least one complex of formula (I) as defined above in a method of producing hydrogen. Preferably, the complex of formula (I) is used in conjunction with a substrate of formula (II) as defined above.

Another aspect of the invention relates to a method of using a hydrogen generation system as defined above which comprises modulating the hydrogen pressure in said system so as to modulate activity of the at least one complex of formula (I).

The present invention is further illustrated by way of the following non-limiting examples, and with reference to the following Figures, wherein:

Figure 1 shows the results of a pressure reactor study of hydrogen equivalents released versus time (h), for the dehydrogenation of ammonia borane in THF at 42°C with (i) compound 6k, and (ii) catalyst 7. The third trace is for the control experiment carried out in THF in the absence of catalyst.

Figure 2 shows the results of a pressure reactor study of hydrogen equivalents released versus time (h), for the dehydrogenation of ammonia borane in $BmimBF_4$ or BmimCl at 74°C with compound 6e versus controls.

Figure 3 shows the results of a pressure reactor study of hydrogen equivalents released versus time (h), for the dehydrogenation of DMAB in THF at room temperature with (i) compound 6e, (ii) compound 6k, and (iii) catalyst 7, versus control (absence of catalyst).

Figure 4 shows the results of a pressure reactor study of hydrogen equivalents released versus time (h), for the dehydrogenation of DMAB in THF at 42°C for catalysts 6e, 6g, 6j, 6k and catalyst 7 versus control (absence of catalyst).

Figure 5 shows the results of a pressure reactor study of hydrogen equivalents released versus time (h), for the solvent-free dehydrogenation of DMAB at 42°C with catalyst 6e and catalyst 7 versus control (absence of catalyst).

Figure 6 shows the results of a pressure reactor study of hydrogen equivalents released versus time (h), for the dehydrogenation of DMAB in THF at room temperature with catalyst 6e under non-protective atmosphere versus control (protective atmosphere, and absence of catalyst).

Figures 7a and 7b show the results of a pressure reactor study of hydrogen equivalents (based on the amounts of substrate) released versus time (h), for the dehydrogenation of DMAB in THF 42°C with catalyst 6e under addition of further aliquots of DMAB/THF solution.

Figure 8 shows the structure of (η^6-benzene)-ruthenium(II)-κ^2*N*,*N*'-*N*,*N*'-bis(2-methylthiophenyl)-1,3-diketiminato chloride (6a).

Figure 9 shows the structure of (η^6-benzene)-ruthenium(II)- κ^2*N*,*N*'-*N*,*N*'-bis(2-methylthiophenyl)-1,3-diketiminato trifluoromethanesulfonate (6e). The anion is omitted for clarity.

Figure 10 shows the results of a pressure reactor study of hydrogen equivalents released versus time (h), for the dehydrogenation of DMAB in THF at 42°C for catalysts 11a, 11c, 11d, 11e, 11f and catalyst 7 versus control (absence of catalyst).

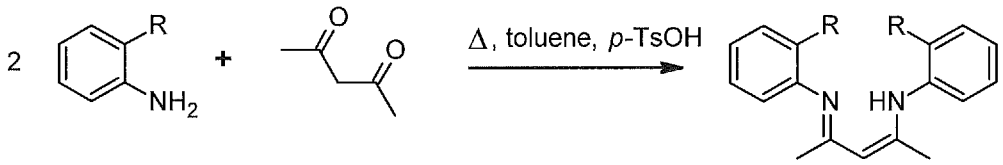
EXAMPLES

Example 1: Preparation of Catalyst

General procedures

The synthesis of the starting materials and the catalysts was carried out under a purified N_2 atmosphere with standard Schlenk techniques, whereas subsequent synthesis and manipulations of all products and reagents were performed in a dry box with a N_2 atmosphere containing less than 1 ppm of O_2 and H_2O and equipped with a vacuum outlet. All glassware was pre-dried and the flasks underwent several purge/refill cycles before the introduction of solvents or reagents. All solvents were dried according to literature procedures involving distillation over the appropriate drying agents and then stored in Schlenk flasks equipped with teflon stopcocks. Celite powder for filtration was kept in an oven at 130 °C prior to use. All other reagents and gases (technical grade) were purchased from commercial sources and used as received if not specified differently. All reactions involving silver salts were carried out in the dark (i.e., vessels were covered with aluminium foil). NMR spectra were recorded using either a Varian 300, 400, 500 or 600 MHz instruments. If necessary, ^{1}H (COSY, NOE), ^{13}C (HMBC and HSQC) one- and two- dimensional spectra were used to assign molecular connectivity and conformation in solution. Deuterated dichloromethane was distilled over CaH_2 and stored in the glove-box. Anhydrous THF-d_8 was purchased in sealed ampoules from Apollo Scientific and used as received. Chemical shifts for ^{1}H, ^{13}C, ^{19}F, and ^{11}B spectra were referenced to Me_4Si or to the appropriate solvent. ESI mass spectra were recorded using a Micromass Quattro micro instrument.

Examples for Synthesis of Ligands



1a: R = SCH_3
1b: R = SCH_2CH_3
1c: R = OCH_3

2a: R = SCH_3
2b: R = SCH_2CH_3
2c: R = OCH_3

Scheme 1

Example 1: Synthesis of Ligand 2a (Scheme 1)

N,N'-Bis(2-methylthiophenyl)-2,4-dimethyl-1,3-diketimine (**2a**) CAS 1198159-02-2

Compound **2a** has been described by Pfirrmann *et* al (Z. Anorg. Allg. Chem. 2009, 635, 312-316). We describe a slightly modified procedure with improved yield.

Acetylacetone (1.14 mL, 11.1 mmol) and p-toluenesulfonic acid monohydrate (4.23 g, 22.2 mmol) were added to a 3-neck round-bottom flask with a Dean-Stark apparatus connected. Degassed toluene (150 mL) and 2-methylthioaniline **1a** (3.35 mL, 26.75 mmol) were added to give a green solution, and the mixture refluxed at 150°C for 24 hours. The resulting yellow solution was cooled, and solvent removed. The resulting oil was taken up in dichloromethane (100 ml) and stirred with a solution of sodium carbonate (40 g in 100 ml H_2O) for 30 minutes. The organic layer was separated and the aqueous layer extracted with dichloromethane (3 x 50 mL), the organic layers were combined, washed with brine, and dried over magnesium sulfate. The solvent was removed to give a yellow oil. Recrystallization from methanol gave **2a** as yellow crystals (2.41 g, 64 %).

^1H & ^{13}C NMR analytical data as described in the literature. Anal. Found [Calc.] C: 66.95 [66.64], H: 6.54 [6.48], N: 8.05 [8.18]. ESI-MS (25° C, CH_3CN), (m/z) positive mode 343.08 [parent + H^+, 100%].

Example 2: Synthesis of Ligand 2b (Scheme 1)

*N,N'-Bis(2-ethylthiophenyl)-2,4-dimethyl-1,3-diketimine (**2b**)*

The synthesis follows the synthesis for **2a** by Pfirrmann *et* al (Z. Anorg. Allg. Chem. 2009, 635, 312-316). Acetylacetone (1.98 g, 19.7 mmol) and p-toluenesulfonic acid monohydrate (3.76 g, 19.7 mmol) were added to a 3-neck round bottom flask with a Dean-Stark apparatus connected. Degassed toluene (150 mL) and 2-ethylthioaniline **1b** (6.06 g, 39.55 mmol) were added to give a brown solution, and the mixture refluxed at 150 °C for 24 hours. The resulting purple solution was cooled, and solvent removed. Saturated sodium carbonate (40 g in 200 mL water) and dichloromethane (200 mL) was added to this and stirred for 30 minutes, to give an orange solution which was extracted with dichloromethane (3 x 50 mL), the organic layers were combined, washed with brine, and dried over magnesium sulfate. The solvent was removed to give a yellow oil. A filtration on silica gel was carried out to remove monosubstituted compound with pentane to give **2b** as yellow oil (3.3 g, 46%) as a mixture of two isomers.

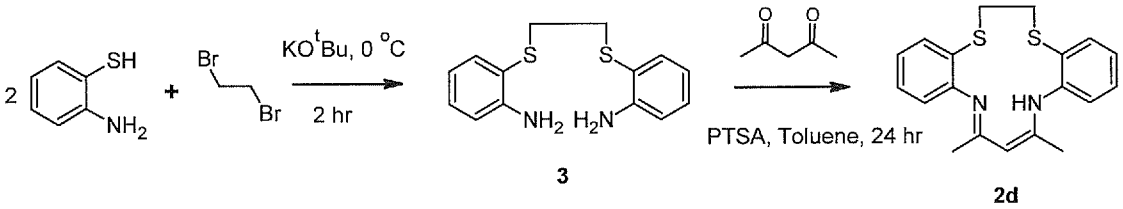
^1H NMR (400 MHz, $CDCl_3$) δ ppm: 1.21 (td, 6H, J = 7.1 Hz, 3.9 Hz, CH_2CH_3), 1.92 (s, 6H, $NCCH_3$), 2.83 (q, 4H, J = 7.4H, 2 x CH_2), 3.70 (q, 4H, J = 7.0 Hz, 2 x CH_2), 4.94 (s,

1H, β-C*H*), 7.0 (m, 8H, Ar-C*H*), 12.55 (br s, 1H, N*H*). ESI-MS (25° C, CH_2Cl_2), (m/z) positive mode 371.54 [parent + H^+, 100%].

Example 3: Synthesis of Ligand 2c (Scheme 1)

N,N'-Bis(2-methoxyphenyl)-2,4-dimethyl-1,3-diketimine (**2c**) CAS 613685-98-6

Compound **2c** has been synthesized according to the procedure described by Carey *et* al (Dalton Trans. 2003, 1083-1093). The analytical data correspond to the literature.



Scheme 2

Example 4: Synthesis of Ligand 2d (Scheme 2)

*Synthesis of 2,2'-(Ethane-1,2-diyldisulfanediyl)dianiline (**3**) CAS 52411-33-3*

The synthesis of **3** has been described by Chandra *et* al (Transition Metal Chemistry 29: 269–275, 2004). We describe a slightly modified procedure with improved yield.

2-Aminothiophenol (2.50 g, 20 mmol) was stirred in dry ethanol (50 mL) and cooled in ice bath. Potassium *t*-butoxide (2.25 g, 20 mmol) was added portion wise to the solution over 15 minutes and the mixture was stirred for further 45 minutes. 1,2-Dibromoethane (0.864 mL, 10 mmol) was added dropwise to the reaction mixture over 15 minutes. The mixture was allowed to warm at room temperature and then stirred for further 45 minutes. The reaction mixture was filtered, and the filtrate was evaporated to dryness in vacuo. The resulting residue was treated with dichloromethane 100 mL and filtered, and the filtrate was evaporated to dryness under vacuum to give white product **3** (Yield = 2.51 g, 91 %).

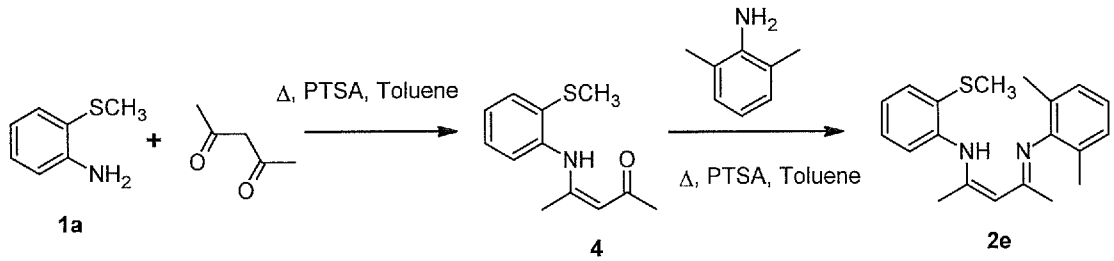
^{1}H NMR (25°C, 500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.11 (td, *J* = 7.6, 1.5 Hz, 1H), 6.70 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.66 (td, *J* = 7.3, 1.3 Hz, 2H), 2.86 (s, 4H).

*Synthesis of **2d***

p-Toluenesulfonic acid monohydrate (1.43 g, 7.48 mmol) was added to a round bottom flask and set up with Dean-Stark apparatus and the flask was put under nitrogen. Toluene (120, degassed) was added to the solid and then 2,4-pentanedione (375 mg, 3.74 mmol) and **3** (1.0 g, 3.74 mmol) were added and the mixture was refluxed for 20

hours at 140 °C. On addition of the aniline derivative the solution went yellow and after 20 hours reflux the solution was bright yellow with a yellow solid. The solvent was removed, and saturated sodium carbonate solution (100 mL) was added to neutralize the acid. It was then extracted with 150 mL dichloromethane and the organic layer was reduced down to 10 mL. Recrystallisation from cold methanol (20 mL) yielded **2d** as a yellow powder (640 mg, 50% yield).

^{1}H NMR (25°C, 300 MHz, $CDCl_3$) δ (ppm): 12.52 (s, 1H, N*H*), 6.87 – 7.04 (m, 8H, Ar C*H*), 4.88 (s, 1H, β-C*H*), 2.85 (s, 4H, SCH_2), 1.85 (s, 6H, -CH_3). ^{13}C NMR (25°C, 101 MHz, $CDCl_3$) δ (ppm): 159.85 (N=*C*), 144.99 (N-*C*), 129.04, 126.37, 124.11, 123.36 (Ar *C*), 97.76 (N=C-*C*H), 31.75 (S-*C*H_2), 20.96(N=C-*C*H_3).



Scheme 3

Example 5: Synthesis of Ligand 2e (Scheme 3)

*Synthesis of **4***

This compound has been described before by Hiraki et al (Bull. Chem. Soc. Japan, 1983, 56, 1410-13). We present an alternative synthesis. Acetylacetone (4.00 g, 39.95 mmol) and p-toluenesulfonic acid monohydrate (0.20 g, 1.05 mmol) were added to a 3-neck round bottom flask with a Dean-Stark apparatus connected. Degassed toluene (150 mL) and 2-methylthioaniline **1a** (5 mL, 39.55 mmol) were added to give a red solution, and the mixture refluxed at 150 °C for 24 hours. The resulting purple solution was cooled and extracted with diethyl ether (200 mL). The organic layers were dried over magnesium sulfate. The solvent was removed to give a yellow oil which was recrystallized from ethanol to give **4** as yellow powder (5.89 g, 67%) as a mixture of two isomers.

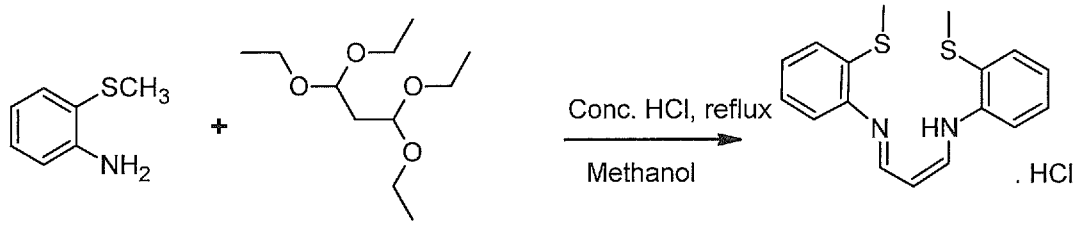
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.87 (s, 3H, OCCH_3), 2.11 (s, 3H, NCCH_3), 2.41 (s, 3H, SCH_3), 5.23 (s, 1H, β-C*H*), 7.09 (m, 1H, *o*-Ar H), 7.12 (m, 1H, *p*-Ar H), 7.20 (m, 2H, *m*-Ar H) 12.26 (br s, 1H, N*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 15.2 (OC*C*H_3), 19.5 (NC*C*H_3), 29.2 (S*C*H_3), 97.5 (β-*C*H), 125.2, 126.2, 126.8, 127.1 (Ar *C*H), 136.1 (Ar *C*S), 136.4 (Ar *i-C*), 160.8 (*C*=N), 196.4 (*C*=O).ESI-MS (25° C, CH_2Cl_2), (m/z) positive mode

222.095 [parent + H^+, 100%]. Anal. Found [Calc.] C: 65.19 [65.12], H: 6.76 [6.83], N: 6.23 [6.34].

Synthesis of **2e**

4 (4.00 g, 18.1 mmol) and p-toluenesulfonic acid monohydrate (3.44 g, 18.1 mmol) were added to a 3-neck round bottom flask with a Dean-Stark apparatus connected. Toluene (150 mL) and 2,6 dimethylaniline (2.19 g, 18.1 mmol) were added to give a yellow mixture which was refluxed at 150 °C for 24 hours. The resulting solution was cooled, and solvent removed. Saturated sodium carbonate (40 g in 200 mL water) and dichloromethane (200 mL) was added to this and stirred for 30 minutes, to give an orange solution which was extracted with dichloromethane (3 x 50 mL), the organic layers were combined, washed with brine, and dried over magnesium sulfate. The solvent was removed to give a yellow oil. A filtration on silica gel was carried out to remove monosubstituted compound with pentane to give **2e** as yellow oil (3.05 g, 52%) as a mixture of isomers.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.70 (s, 3H, isomer CH_3), 1.93 (s, 3H, C*H*$_3$), 2.18 (s, 3H, C*H*$_3$), 2.24 (s, 6H, 2 x phenyl CH_3), 2.37 (s, 3H, SC*H*$_3$), 4.93 (s, 1H, β-C*H*), 7.09 (m, 1H, *o*-Ar H), 7.12 (m, 1H, *p*-Ar H), 7.20 (m, 2H, *m*-Ar H) 12.25 (br s, 1H, N*H*).



1a **2f**

Scheme 4

Example 6: Synthesis of Ligand 2f (Scheme 4)

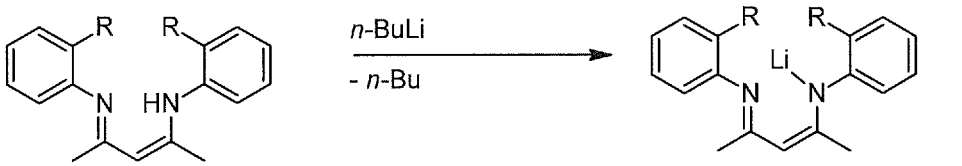
*N,N'-Bis(2-methylthiophenyl)-1,3-diketimine hydrochloride (**2f**)*

1,1,3,3-Tetraethoxypropane (1.0 g, 4.5 mmol) and 2-(methylthio)aniline **1a** (1.19 g, 9.0 mmol, 2 equiv.) were dissolved in a small volume of hot methanol and the solution was acidified with a 5 mL of concentrated hydrochloric acid diluted 1:1 with methanol (5 mL). A yellow solid of the tri-hydrochloric acid product separated immediately while stirring at room temperature, washed with methanol-ether mixture, filtered and dried under reduced pressure. The yellow solid was dissolved in saturated aq. sodium carbonate solution while stirring and then dropwise addition of triethylamine until the yellow solid

dissolved completely. The aq. solution was extracted with dichloromethane (x 3), washed with brine, dried with magnesium sulphate, and the solvent was reduced in vacuo to yield **2f** as a dark brown oil. Yield = 1.54 g, 98%.

^{1}H NMR (25°C, 300 MHz, $CDCl_3$) δ (ppm): 11.90 (s, 1H, N*H*), 7.59 (d, *J* = 5.2 Hz, 2H, α-C*H*), 7.29 (d, *J* = 7.9 Hz, 2H, Ar C*H*), 7.16 (d, *J* = 7.8 Hz, 2H, Ar C*H*), 7.11 – 6.95 (m, 4H, Ar C*H*), 5.18 (t, *J* = 6.2 Hz, 1H, β-C*H*), 2.38 (m, 6H, SCH_3). ^{13}C NMR (25°C, 101 MHz, $CDCl_3$) δ (ppm): 148.86 (N=*C*), 146.38 (N-*C*), 129.42, 128.48, 126.62, 123.86, 116.62 (Ar-C), 96.43 (N=C-CH), 16.56 (S-*C*).

Examples for Lithiation of Ligands



2a: R = SCH_3
2b: R = SCH_2CH_3
2c: R = OCH_3
2d: RR = SCH_2CH_2S

5a: R = SCH_3
5b: R = SCH_2CH_3
5c: R = OCH_3
5d: RR = SCH_2CH_2S

Scheme 5

Example 7: Synthesis of Lithiated Ligand 5a (Scheme 5)

Lithium N,N'-bis(2-methylthiophenyl)-1,3-diketiminate

2a (1.85 g, 5.40 mmol) was added to a dried Schlenk. Dry degassed pentane was transferred via cannula, and the pale yellow mixture cooled on ice. *n*-BuLi (3.4 mL, 1.6M in hexanes) was added dropwise to give a bright yellow mixture. After stirring for 3 hours at room temperature, the solid was filtered, washed with dry pentane and dried to give **5a** as a bright yellow powder (1.21 g, 64%).

^{1}H NMR (400 MHz, C_6D_6) δ ppm: 1.90 (s, 6H, 2 x $NCCH_3$), 1.99 (s, 6H, 2 x SCH_3), 4.77 (s, 1H, β-C*H*), 6.82 (m, 2H, Ar *p*-C*H*), 6.90 (m, 2H, Ar *o*-C*H*), 7.08 (m, 2H, Ar *m*-C*H*), 7.10 (m, 2H, Ar *m*-C*H*). ^{13}C NMR (101 MHz, C_6D_6) δ ppm: 16.2 (2 x $NCCH_3$), 22.9 (2 x SCH_3), 98.1 (β-CH), 121.7, 121.9, 123.9, 124.0, (Ar CH), 127.0 (Ar CS), 130.4 (Ar *i*-C), 152.8 (*C*=N).

Example 8: Synthesis of Lithiated Ligand 5b (Scheme 5)

Lithium N,N'-bis(2-ethylthiophenyl)-1,3-diketiminate

2b (3.0g, 8.1mmol) was added to a dried Schlenk. Dry degassed pentane was transferred via cannula, and the pale yellow mixture cooled on ice. *n*-BuLi (6.0 mL, 1.6M in hexanes) was added dropwise to give a bright red mixture. After stirring for 3 hours at room temperature, the resulting solid was filtered, washed with dry pentane and dried to give **5b** as an orange powder (1.67g, 55%).

^{1}H NMR (400 MHz, C_6D_6) δ ppm: 1.00 (t, 6H, *J* = 7.3 Hz, CH_2CH_3), 1.86 (s, 6H, $NCCH_3$), 2.43 (br s, 4H, 2 x CH_2), 4.63 (s, 1H, β-C*H*),6.37 (br s, 1H, Ar *o*-C*H* to N), 6.68 (br s, 1H, Ar *o*-C*H* to N), 6.92 (m, 2H, Ar *p*-C*H* to N), 7.22 (br s, 4H, Ar *m*-C*H* to N). ^{13}C NMR (101 MHz, C_6D_6) δ ppm: 14.15, 22.97, 27.77, 122.52, 125.18, 153.22. *Not all signals were apparent.*

Example 9: Synthesis of Lithiated Ligand 5c (Scheme 5)

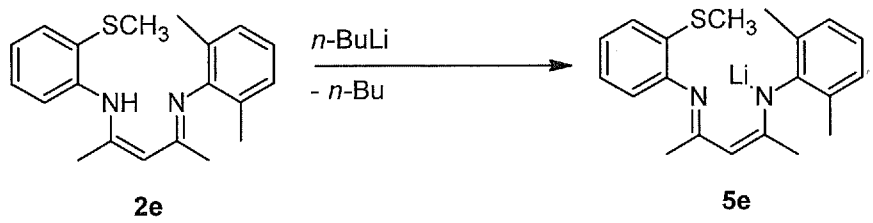
Lithium N,N'-bis(2-methoxyphenyl)-1,3-diketiminate

2c (1.50 g) was added to a dried Schlenk. Dry degassed pentane was transferred via cannula, and the pale yellow mixture cooled on ice. *n*-BuLi (3.4 ml, 1.6M in hexanes) was added dropwise to give a bright yellow mixture. After stirring for 3 hours at room temperature, the solid was filtered, washed with dry pentane and dried to give **5c** as a bright yellow powder (1.09 g).

1H NMR (400 MHz, C_6D_6) δ ppm: 1.97 (s, 6H, $NCCH_3$), 3.07 (s, 6H, OCH_3), 4.81 (s, 1H,β-C*H*), 6.39 (d, *J* = 8.0 Hz, 2H, Ar *o*-H to O), 6.77 (td, *J* = 7.9, 1.6 Hz, 2H, Ar *p*-H to N), 6.86 (td, *J* = 7.6, 1.1 Hz, 2H, Ar *m*-H to N), 6.95 (dd, *J* = 7.7, 1.3 Hz, 2H, Ar *o*-H to N).

Example 10: Synthesis of Lithiated Ligand 5d (Scheme 5)

To 356 mg of **2d** (1.05 mmol) in a 100 mL schlenk flask was added 10 mL of dry pentane under nitrogen at –98°C. While stirring, a solution of 1.1 equivalent of 1.6 M *n*-BuLi in hexane (0.7 mL, 1.15 mmol) was added slowly dropwise, and instantly the solution changed from a bright yellow to a light yellow color. The reaction mixture was stirred at room temperature for 3 hours and the solvent was reduced under vacuum to a light yellow solid and washed with pentane to get complex **5d** (341 mg, 0.945 mmol, 90%). The lithiated complex **5d** was used as synthesised without further analysis.



2e **5e**

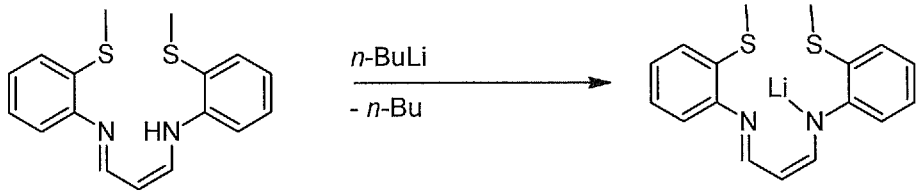
Scheme 6

Example 11: Synthesis of Lithiated Ligand 5e (Scheme 6)

Lithium N-(2,6-dimethylphenyl)-N'- (2-methoxyphenyl)-1,3-diketiminate

2e (3.05 g, 9.40 mmol) was added to a dried Schlenk. Dry degassed pentane was transferred via cannula, and the pale yellow mixture cooled on ice. *n*-BuLi (6.4 mL, 1.6M in hexanes) was added dropwise to give a bright yellow mixture. After stirring for 3 hours at room temperature, the solvent was removed to give **5e** as a bright yellow powder (3.02 g, 97%) as a mixture of isomers.

^{1}H NMR (400 MHz, C_6D_6) δ ppm: 1.70 (s, 3H, isomer C*H*$_3$), 1.72 (s, 3H, isomer C*H*$_3$), 1.74 (s, 3H, isomer C*H*$_3$), 2.03 (s, 3H, SC*H*$_3$), 2.22 (s, 6H, 2 x C*H*$_3$), 4.78 (s, 1H, β-C*H*), 6.57 (m, 1H, Ar C*H*), 6.75 (m, 1H, Ar C*H*), 6.84 (m, 1H, Ar C*H*), 6.95 (m, 2H, Ar C*H*) 7.10 (m, 2H, Ar C*H*).



2f **5f**

Scheme 7

Example 12: Synthesis of Lithiated Ligand 5f (Scheme 7)

2f (1.0g, 3.2 mmol) was added to a dried Schlenk flask. Dry degassed pentane was transferred via cannula, and the pale brown mixture was cooled on ice. *n*-BuLi (2.2 mL, 1.6M in hexanes) was added dropwise. After stirring for 3 hours at room temperature, the resulting solid was filtered, washed with dry pentane and dried to give **5f** as a brown powder (0.7g, 70%).

^{1}H NMR (400 MHz, C_6D_6) δ ppm: 7.90 (d, *J* = 6.3, 2H, α-C*H*), 7.26 (dd, *J* = 7.7, 1.5, 2H, Ar *m*-C*H* to N), 7.11 (ddd, *J* = 8.1, 7.1, 1.5, 2H, Ar m-C*H* to N), 7.04 (dd, *J* = 8.1, 1.5, 2H, Ar *o*-C*H* to N), 6.83 (ddd, *J* = 7.7, 7.1, 1.5, 2H, Ar *p*-C*H* to N), 5.06 (t, *J* = 6.3, 1H, β-C*H*), 1.87 (s, 6H, SC*H*$_3$). ^{13}C NMR (101 MHz, C_6D_6) δ ppm: 154.5 (α-CH), 154.4 (N-

C_{Ar}), 131.70 (Ar m-*C*H to N), 129.41 (Ar m-*C*H to N), 128.30 (*C*-SCH_3), 122.31 (Ar *p*-*C*H to N), 117.21 (Ar *o*-*C*H to N), 96.00 (α-*C*H), 17.72 (SCH_3).

Examples for Metal Complexes

It is understood that generally at some point, the donor ligand D dissociates in (ref. structure II) solution to form the active catalytic species, although at some point re-association cannot be ruled out. Some of the compounds (ref. Example 14, 16, 17) are isolated after synthesis as a mixture of the complex with the donor ligand D and the complex where D has been lost. These mixtures were used without further separation in the dehydrogenation experiments.

5a $\xrightarrow{a)}$ 6a

5b $\xrightarrow{a)}$ 6b + 6c

5c $\xrightarrow{a)}$ 6d

5a $\xrightarrow{b)}$ 6e + 6f

5b $\xrightarrow{b)}$ 6g + 6h

5c $\xrightarrow{b)}$ 6i

5a $\xrightarrow{c)}$ 6j

5a $\xrightarrow{d)}$ 6k

5a $\xrightarrow{e)}$ 6l

6l $\xrightarrow{f)}$ 6m

5d $\xrightarrow{e),f)}$ 6n

5e $\xrightarrow{a)}$ 6o

5e $\xrightarrow{b)}$ 6p

5f $\xrightarrow{g)}$ 6q + 6r

a) $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$, CH_2Cl_2

b) $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$, NaOTf, CH_2Cl_2

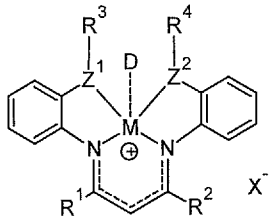
c) $Ru(PPh_3)_3Cl_2$, CH_2Cl_2

d) $Ru(PPh_3)_3Cl_2$, AgOTf, CH_2Cl_2

e) $Ni(DME)Br_2$, CH_2Cl_2

f) $AgPF_6$, CH_2Cl_2

g) $Ru(PPh_3)_3Cl_2$, NaOTf, CH_2Cl_2



6a: M = Ru; D = η^6–C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Cl^-

6b: M = Ru; D = η^6–C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; X^- = Cl^-

6c: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; X^- = Cl^-

6d: M = Ru; D = η^6–C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; X^- = Cl^-

6e: M = Ru; D = η^6–C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

6f: M = Ru; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

6g: M = Ru; D = η^6–C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; X^- = OTf^-

6h: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; X^- = OTf^-

6i: M = Ru; D = η^6–C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; X^- = OTf^-

6j: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Cl^-

6k: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

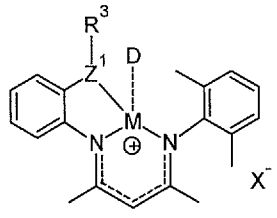
6l: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Br^-

6m: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = PF_6^-

6n: M = Ni; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^3R^4 = CH_2CH_2; X^- = PF_6^-

6q: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-2} = H; R^{3-4} = CH_3; X^- = OTf^-

6r: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-2} = H; R^{3-4} = CH_3; X^- = Cl^-



6o: M = Ru; D = η^6–C_6H_6; Z^1 = S: R^3 = CH_3: X^- = Cl^-

6p: M = Ru; D = η^6–C_6H_6; Z^1 = S: R^3 = CH_3: X^- = OTf^-

Scheme 8

Example 13: Synthesis of Ruthenium Complex 6a (Scheme 8)

5a (0.50 g, 1.44 mmol) and $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$ (0.36 g, 0.72 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to

give a dark red/brown solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark red solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give **6a** as a dark red powder (0.32 g, 41 %). Crystals suitable for x-ray were grown by slow diffusion of dichloromethane into a pentane solution of **6a**.

^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 1.62 (s, 6H, NCC*H*$_3$), 2.48 (s, 6H, SC*H*$_3$), 4.54 (s, 1H, β-C*H*), 4.70 (s, 6H, C_6H_6), 7.20 (m, 6H, Ar-*H*), 7.68 (m, 2H, Ar-*H*). ^{13}C NMR (101 MHz, CD_2Cl_2) δ ppm: 14.3 (CCH_3), 23.9 (SCH_3), 86.0 (C_6H_6), 96.0 (β-CH), 123.1, 124.9, 125.3, 126.7 (Ar CH), 143.6 (Ar *C*S), 156.8 (Ar *i-C*), 161.7 (*C*=N). Anal. Found [Calc.] C: 54.15 [53.99], H: 4.94 [4.89], N: 5.25 [5.03].

Example 14: Synthesis of Ruthenium Complex 6b (Scheme 8)

5b (0.40g, 1.06 mmol) and $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$ (0.26g, 0.53 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to give a dark red/brown solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark red solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vacuo. The residue was washed with dry pentane, which was decanted and the solid dried to give predominantly **6c** with trace **6b** as a dark red powder (0.18g, 34 %). ^{1}H NMR (Signals for ; 400 MHz, CD_2Cl_2) δ ppm: 1.21 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 1.43 (t, 3H, *J* = 7.3 Hz, SCH_2CH_3), 1.89 (s, 6H, NCC*H*$_3$), 2.81 (dd, 2H, *J* = 7.4Hz, 14.7 Hz, SC*H*$_2$), 3.03 (m, 2H, SC*H*$_2$), 6.28 (s, 1H, β-C*H*), 6.91 -7.68 (m, 8H, Ar C*H*). ^{13}C NMR (101 MHz, CD_2Cl_2) δ ppm: 14.3, 21.1, 23.9, 24.9, 26.8, 86.1, 87.2, 97.9, 123.6, 123.9, 124.6, 125.4, 126.2, 128.2, 128.6, 144.9, 160.6. ESI-MS (25° C, CH_2Cl_2), (m/z) positive mode 549.41 [**6b**, 30%], 471.39 [**6c**, 70%].

Example 15: Synthesis of Ruthenium Complex 6d (Scheme 8)

5c (0.40 g) and $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$ (0.32 g) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to give a dark red/brown solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark red solution was filtered through Celite, washed with dry DCM and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give complex **6d** as a dark purple powder (0.52 g).

^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 1.62 (s, 6H, NCC*H*$_3$), 4.00 (s, 6H, OC*H*$_3$), 4.45 (s, 1H, β-C*H*), 4.59 (s, 6H, C_6H_6), 7.02 (m, 4H, Ar C*H*), 7.19 (m, 2H, Ar C*H*), 7.91 (m, 2H, Ar C*H*).

Example 16: Synthesis of Ru Complex 6e (Scheme 8)

5a (0.47g, 1.33 mmol), $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$ (0.34g, 0.67 mmol) and sodium triflate (0.26g, 1.50 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to give a brown solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark red solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give the product as a dark red powder (0.71g, 80 %). Crystals suitable for x-ray were grown by slow diffusion (THF). The NMR for this complex shows two species, one containing the coordinated benzene ring (**6e**), and one where benzene has been lost (**6f**). Percentage yield based on complex **6e**. Crystals suitable for x-ray were grown by slow diffusion of dichloromethane into a pentane solution of **6e**.

6e: ^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 2.10 (s, 6H, NCC*H*$_3$), 2.44 (s, 6H, SC*H*$_3$), 6.29 (s, 1H, β-C*H*), 5.24 (s, 6H, C_6H_6), 7.01 (m, 2H, Ar-*H*), 7.10 (m, 6H, Ar-*H*).

6f: ^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 1.79 (s, 6H, NCC*H*$_3$), 2.26 (s, 6H, SC*H*$_3$), 5.87 (s, 1H, β-C*H*), 7.40 (m, 8H, Ar-*H*). ^{13}C NMR (101 MHz, CD_2Cl_2) δ ppm: 14.4, 14.5, 14.8, 20.4, 23.2, 83.5, 86.7, 97.1, 104.2, 119.3, 122.5, 124.0, 124.2, 124.3, 124.8, 125.2, 127.0, 127.9, 128.3, 130.2, 130.6, 132.9, 133.2, 143.1, 156.1, 159.3, 160.6, 164.2.^{19}F NMR (376 MHz, CD_2Cl_2) δ ppm: -78.8 (OTf). Anal. Found [Calc.] C: 47.99 [46.62], H: 4.11 [4.06], N: 4.61 [4.18]. ESI-MS (25° C, CH_2Cl_2), (m/z) positive mode 443.34 [**6f**, 100%], 521.33 [**6e**, 30%].

Example 17: Synthesis of Ru Complex 6g (Scheme 8)

5b (0.40g, 1.06 mmol), $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$ (0.26g, 0.53 mmol) and sodium triflate (0.20g, 1.16 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to give a brown solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark red solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give predominantly complex **6h**, where the benzene ligand has been lost, as a dark red crystalline solid (0.33g, 50 %) with some presence of the title complex **6g** (10 – 40%

varying). ^{1}H NMR (Signals for **6h**; 400 MHz, CD_2Cl_2) δ 1.21 (t, 3H, J = 7.4 Hz, CH_2CH_3), 1.39 (m, 3H, CH_2CH_3), 1.89 (s, 6H, $NCCH_3$), 2.79 (m, 2H, CH_2), 3.03 (m, 2H, CH_2), 6.00 (s, 1H, β-C*H*), 6.91 - 7.45 (m, 8H, Ar-*H*). ^{13}C NMR (101 MHz, CD_2Cl_2) δ ppm: 14.3, 21.1, 23.9, 26.8, 84.0, 87.3, 98.0, 123.9, 124.6, 126.2, 128.6, 128.8, 144.9, 160.6. ^{19}F NMR (376 MHz, CD_2Cl_2) δ ppm: -78.8. ESI-MS (25° C, CH_2Cl_2), (m/z) positive mode 471.39 [parent, 60%].

Example 18: Synthesis of Ru Complex 6i (Scheme 8)

(0.35g, 0.67 mmol) **5c** and sodium triflate (0.138g, 0.80 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 ml) was transferred via cannula to give a brown solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark red solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vacuo. The residue was washed with dry pentane, which was decanted and the solid dried to give **6i** as a red/orange powder (0.30g, 70 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 2.20 (s, 6H, $NCCH_3$), 4.00 (s, 6H, OCH_3), 5.15 (s, 6H, C_6H_6), 6.41 (s, 1H, β-C*H*), 7.21 (m, 4H, Ar-*H*), 7.31 (m, 2H, Ar-*H*) 7.49 (m, 2H, Ar-*H*).

Example 19: Synthesis of Ru Complex 6j (Scheme 8)

To **5a** (156 mg, 0.438 mmol) was added a solution of complex $[Ru(PPh_3)_3Cl_2]$ (420 mg, 0.438 mmol) in dry dichloromethane (10 mL) under nitrogen at room temperature, and instantly the solution changed to a purple color. The reaction mixture was stirred for 14 h under nitrogen at room temperature. Afterward the purple solution was filtered through a frit containing at least 1 cm pad of Celite. The Celite was washed with dichloromethane until the filtrate was colorless. The volume of the filtrate was reduced, under vacuum, to 2 mL, and 25 mL of *n*-pentane was added to precipitate a purple-colored microcrystalline powder. The solution was decanted from the solid and dried under vacuum for several hours. The product was stable in air as a purple solid complex **6j** (yield = 304 mg, 0.411 mmol, 94 %).

^{1}H NMR (25°C, 300 MHz, $CDCl_3$) δ (ppm): 7.31 (d, J = 9.5 Hz, 6H, PPh_3 *o*-H), 7.23 (t, J = 3.5 Hz, 6H, PPh_3 *m*-H), 7.17 (d, J = 6.9 Hz, 3H, PPh_3 *p*-H), 6.97 (m, 4H, Ar-C*H*), 6.80 (m, 2H, Ar-C*H*), 4.56 (s, 1H, β-C*H*), 2.80 (s, 6H, SCH_3), 1.81 (s, 6H, α-CH_3). ^{13}C NMR (25°C, 101 MHz, $CDCl_3$) δ (ppm): 158.88 (*C*=N), 154.35 (*C*-N), 133.56, 129.64, 128.44, 127.51, 126.36, 124.08, 121.71 (Ar-*C*), 109.99 (N=C-*C*H), 25.26 (SCH_3), 22.76

(N=CCH_3). ^{31}P NMR (25°C, 121 MHz, $CDCl_3$) δ (ppm): 58.67 (s, *P*Ph_3). TOF MS-ES (25°C, dichloromethane), positive mode (m/z): exp. Mass for C37H36N2PS2ClRu [Parent [M]+ = 740.0821 (100 %), calculated [M]+ = 740.0790 (100 %)]. Elemental analysis: Found [Calculated] for $C_{37}H_{36}ClN_2PRuS_2$. 5 CH_2Cl_2; C: 45.96 [45.59], H: 4.04 [4.11], N: 2.52 [2.59].

Example 20: Synthesis of Ru Complex 6k (Scheme 8)

To **5a** (150 mg, 0.421 mmol) and silver triflate (108 mg, 0.421 mmol) was added a solution of complex [Ru(PPh_3)$_3Cl_2$] (403 mg, 0.421 mmol) in dry 10 mL CH_2Cl_2 under nitrogen at room temperature, and instantly the solution changed to a purple color. The reaction mixture was stirred for 14 h under nitrogen at room temperature. Afterward the purple solution was filtered through a frit containing at least 1 cm pad of Celite. The Celite was washed with dichloromethane until the filtrate was colorless. The volume of the filtrate was reduced, under vacuum, to 2 mL, and 25 mL of *n*-pentane was added to precipitate a purple-colored microcrystalline powder. The solution was decanted from the solid, dried under vacuum for several hours and kept under glove box. The yield of the purple complex **6k** was 95% (340 mg, 0.398 mmol).

1H NMR (400 MHz, CD_2Cl_2) δ (ppm): 7.35 (dd, *J* = 7.7, 1.5, 2H, Ar *m*-C*H* to N), 7.31 – 7.14 (m, 15H, PPh_3), 7.03 (ddd, *J* = 8.4, 7.0, 1.5, 2H, Ar *m*-C*H* to N), 6.91 (dd, *J* = 8.4, 1.5, 2H, Ar *o*-C*H* to N), 6.91 - 6.81 (m, 2H, Ar *p*-C*H* to N), 4.62 (s, 1H, β-C*H*), 2.78 (s, 6H, SCH_3), 1.81 (s, 6H, α-CH_3). ^{13}C NMR (101 MHz, CD_2Cl_2) δ (ppm): 159.53 (*C*=N), 154.97 (N-C_{Ar}), 136.41 (d, $^1J_{PC}$ = 41.2, PPh_3 C_{ipso}), 134.58 (*C*-SCH_3), 134.13 (d, J_{PC} = 8.9, PPh_3 $C_{ortho/meta}$), 129.55 (d, $^4J_{PC}$ = 2.2, PPh_3 C_{para}), 129.38 (Ar *m*-CH to N), 128.14 (d, J_{PC} = 8.9, PPh_3 $C_{ortho/meta}$) 126.80 (Ar *m*-CH to N), 124.32 (Ar *o*-CH to N), 122.12 (Ar *p*-CH to N) 113.97 (β-CH), 25.56 (SCH_3), 22.92 (N=CCH_3).^{1}P NMR (121 MHz, CD_2Cl_2) δ (ppm): 58.42 (s, *P*Ph_3). ^{19}F NMR (282 MHz, CD_2Cl_2) δ (ppm): -78.84 (s, -O_3SCF_3).

Example 21: Synthesis of Ni Complex 6m (Scheme 6)

Intermediate **6l** CAS 1198159-01-1 has been described by Pfirrmann *et* al (Z. Anorg. Allg. Chem. 2009, 635, 312-316). To **5a** (250 mg, 0.717 mmol) was added a suspensions of orange complex [Ni(DME)Br_2] (221.5 mg, 0.717 mmol) in a dry 10 mL CH_2Cl_2 under nitrogen at room temperature, and after 10 minutes the solution changed to a dark green color. The reaction mixture was stirred for 14 h under nitrogen at room temperature. Afterward the green solution was filtered through a frit containing at least 1 cm pad of Celite. The Celite was washed with CH_2Cl_2 until the filtrate was colorless.

The volume of the filtrate was reduced, under vacuum, to 2 mL, and 25 mL of n-pentane was added to precipitate a green colored microcrystalline powder. The solution was decanted from the solid and dried under vacuum for several hours. The product was treat as unstable in air as a green solid complex **6l** (yield = 201 mg, 0.416 mmol, 58 %). Without any further analysis of above product, silver hexafluorophosphate (105 mg, 0.416 mmol) was added in to the dichloromethane (10 mL) solution of **6l** (201 mg, 0.416 mmol) and the reaction mixture was stirred for 14 h under nitrogen at room temperature. Afterward the dark green solution was filtered through a frit containing at least 1 cm pad of Celite. The Celite was washed with CH_2Cl_2 until the filtrate was colorless. The volume of the filtrate was reduced, under vacuum to precipitate a green colored microcrystalline powder of **6m** (yield = 160 mg, 0.333 mmol, 80%). The product was confirmed by HRMS due to its paramagnetic behaviour.

TOF MS-ES (25°C, CH_2Cl_2), positive mode (m/z): Exp. Mass for $[C_{19}H_{21}F_6N_2NiPS_2]$: [Parent [M]+ = 544.1911 (100 %), calculated [M]+ = 544.0141 (100 %)].

Example 22: Synthesis of Ni Complex 6n (Scheme 8)

To **5d** (356 mg, 1.05 mmol) was added a suspension of orange complex $[Ni(DME)Br_2]$ (324 mg, 1.05 mmol) and $AgPF_6$ (265.5 mg, 1.05 mmol) in a dry 10 mL dichloromethane under nitrogen at room temperature, and after 10 minutes the solution changed to a dark brown color. The reaction mixture was stirred for 14 h under nitrogen at room temperature. Afterward the brown solution was filtered through a frit containing at least 1 cm pad of Celite. The Celite was washed with dichloromethane until the filtrate was colorless. The volume of the filtrate was reduced under vacuum to precipitate a brown colored microcrystalline powder. The solution was decanted from the solid and dried under vacuum for several hours. The product was treat as unstable in air as a brown solid complex **6n** (yield = 251 mg, 0.462 mmol, 44 %). The product was confirmed by HRMS due to its paramagnetic behaviour.

TOF MS-ES (25°C, dichloromethane), positive mode (m/z): Exp. Mass for $[C_{19}H_{19}F_6N_2NiPS_2]$: [Parent [M]+ = 543.1212 (100 %), calculated [M]+ = 543.0132 (100 %)].

Example 23: Synthesis of Ru Complex 6o (Scheme 8)

5e (0.40 g, 1.21 mmol) and $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$ (0.30 g, 0.61 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to

give a dark red/brown solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark red solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give **6o** as a pale beige/brown powder (0.26 g, 41 %) as a mixture of isomers.

^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 1.53 (s, 3H, isomer C*H*$_3$), 1.63 (s, 3H, isomer C*H*$_3$), 2.23 (s, 3H, phenyl C*H*$_3$), 2.48 (s, 3H, isomer C*H*$_3$), 2.55(s, 3H, phenyl C*H*$_3$), 4.56 (s, 6H, C_6H_6), 4.73 (s, 1H, β-C*H*), 7.02 (m, 2H, Ar-*H*), 7.18 (m, 4H, Ar-*H*) 7.61 (m, 1H, Ar-*H*).

Example 24: Synthesis of Ru Complex 6p (Scheme 8)

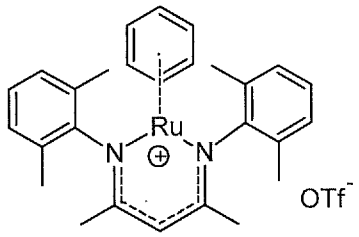
5e (0.40g, 1.21 mmol), $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$ (0.30g, 0.61 mmol) and sodium triflate (0.23g, 1.33 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to give a purple solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark brown solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give **6p** as a golden powder (0.40 g, 51 %) as a mixture of isomers.

^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 1.67 (s, 3H, isomer C*H*$_3$), 2.09 (s, 3H, isomer C*H*$_3$), 2.13 (s, 3H, isomer C*H*$_3$), 2.15 (s, 3H, isomer C*H*$_3$), 2.22 (s, 6H, phenyl 2 x C*H*$_3$), 2.53 (s, 3H, isomer C*H*$_3$), 5.20 (s, 6H, C_6H_6), 6.51(s, 1H, β-C*H*), 7.02 (m, 1H, Ar-*H*), 7.31 (m, 1H, Ar-*H*) 7.40 (m, 2H, Ar-*H*), 7.50 (m, 3H, Ar-*H*). ^{13}C NMR (101 MHz, CD_2Cl_2) δ ppm: 14.1, 15.1, 18.6, 19.0, 19.2, 20.6, 23.4, 23.8 (*C*H$_3$), 84.1 (C6H6), 105.3 (β-*C*H), 124.6, 124.7, 125.5, 127.9, 128.2, 128.6, 129.5, 129.6, 130.1, 132.7 (Ar-*C*), 164.1, 164.7.

Example 25: Synthesis of Ru Complex 6q (Scheme 8)

5f (52 mg, 0.15 mmol), $[Ru(PPh_3)_3Cl_2]$ (144 mg, 0.15 mmol) and sodium triflate (28 mg, 0.16 mmol) were dissolved in dry CH_2Cl_2 (10 mL) under nitrogen and left to stir for 24 h at room temperature. Upon dissolution the color instantly changed from green to purple. The solution was filtered through a 1 cm celite pad and washed with CH_2Cl_2 until the filtrate was colorless. The volume of the filtrate was reduced to 2 mL under vaccum and dry *n*-pentane (25 mL) was added to precipitate complex **6q** as purple-colored powder. The solid was filtered, dried under vacuum and kept in glove box. Yield 80 mg (63%). A small quantity of compound **6r** crystallized as side product (not quantified; structure was identified by X-ray diffraction analysis).

^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm): 7.84 (d, J = 6.9, 2H, α-C*H*), 7.43 – 7.28 (m, 4H, Ar), 7.18 – 6.98 (m, 17H, Ar + PPh_3), 6.94 – 6.81 (m, 2H, Ar *p*-C*H* to N), 5.08 (t, J = 6.9, 1H, β-C*H*), 2.88 (s, 6H, SCH_3). ^{13}C NMR (101 MHz, CD_2Cl_2) δ (ppm): 153.62 (N-C_{Ar}), 144.24 (α-CH), 134.23 (d, J_{PC} = 9.1, PPh_3 $C_{ortho/meta}$), 133.13 (d, $^1J_{PC}$ = 42.7, PPh_3 C_{ipso}), 131.13 (Ar *m*-CH to N), 130.73 (*C*-SCH_3), 129.68 (br, PPh_3 C_{para}), 129.16 (Ar *m*-CH to N), 127.61 (d, J_{PC} = 9.1, PPh_3 $C_{ortho/meta}$), 122.78 (Ar *p*-CH to N), 116.05 (Ar *o*-CH to N), 98.06 (β-CH), 23.19 (SCH_3). ^{1}P NMR (121 MHz, CD_2Cl_2) δ (ppm): 55.14 (s, PPh_3).



7

Scheme 9

Comparative Example 1: Synthesis of Ru Complex 7 (Scheme 9)

(η^6-Benzene)-ruthenium(II)-κ^2N,N'-N,N'-bis(2,6-dimethylphenyl)-1,3-diketiminato trifluoromethanesulfonate

The synthesis and analysis of this catalyst has been described previously by Phillips *et al* (Organometallics 2007, 26, 1120–1122).

Examples for Dehydrogenation Reactions

Example 26: Dehydrogenation of Ammonia Borane in THF with catalyst 6k at 42°C (Figure 1)

A 100 mL Parr 100 bar stainless steel pressure reactor, fitted with an inlet valve (Swagelok SS-ORM2), release valve (Swagelok SS-43GS4), thermocouple, rupture disc, stirrer shaft (Parr A1120HC5), and a 0-100 bar pressure gauge (Impress Sensors & Systems) connected to a Parr 4842 controller unit, was used for the experiment. To avoid contamination of the reactor interior by traces of catalyst, a base/acid cleaned glass liner was used for the experiment. Stirrer and thermocouple probe were sanded prior to each run. The reaction was carried out without stirring as homogeneous mixing was ensured through internal gas evolution. H_2 equivalents respectively to AB substrate were calculated from the recorded pressure data assuming ideal gas behaviour, assuming a total reactor volume (including head space) of 84 mL.

The Parr pressure reactor was flushed with nitrogen and preheated to 42°C using an oil bath prior to the start of the experiment. A glass liner was filled with 0.5 g (16 mmol) of ammonia borane and 0.5 mol% (0.08 mmol, 69 mg) of **6k** under a stream of N_2, inserted into the reactor, and the reactor was sealed. 5 mL of dried/N_2 saturated THF were added through the sampling valve via a gas-tight syringe and the valve was closed.

Comparative Example 2: Dehydrogenation of Ammonia Borane in THF with catalyst 7 at 42°C (Figure 1)

Procedure as in Example 26. Ammonia borane: 1.0 g (32 mmol); catalyst: 0.5 mol%, 0.16 mmol, 102 mg; THF: 10 mL.

Comparative Example 3: Dehydrogenation of Ammonia Borane in THF without catalyst at 42°C (Figure 1)

Procedure as in Example 26. Ammonia borane: 1.0 g (32 mmol); THF: 10 mL.

Example 27: Dehydrogenation of Ammonia Borane in $BmimBF_4$ with catalyst 6e at 74°C (Figure 2)

Following the procedure of Ex. 26, the Parr pressure reactor was preheated to 74°C. A glass liner was filled with 0.5 mol% (0.06 mmol, 42 mg) of **6e** under a stream of N_2, inserted into the reactor, and the reactor was sealed. A solution of ammonia borane (0.39 g, 12.7 mmol) in dry 1-butyl-1-methylimidazolium tetrafluoroborate (2.9 mL) was added through the sampling valve via a gas-tight syringe and the valve was closed.

Example 28: Dehydrogenation of Ammonia Borane in BmimCl with catalyst 6e at 74°C (Figure 2)

Following the procedure of Ex. 26, the Parr pressure reactor was preheated to 74°C. A glass liner was filled with 0.5 mol% (0.06 mmol, 42 mg) **6e**, ammonia borane (0.39 g, 12.7 mmol), and dry 1-butyl-1-methylimidazolium chloride (4 g) under a stream of N_2, inserted into the reactor, and the reactor was sealed.

Comparative Examples 4-5: Dehydrogenation of Ammonia Borane in BmimCl or $BmimBF_4$ without catalyst at 74°C (Figure 2)

Following the procedure of Exp. 27 (Comp. Ex. 4) or Exp. 28 (Comp. Ex. 5) without **6e**.

Example 29: Dehydrogenation of DMAB in THF with 6e at room temperature (Figure 3)

Following the procedure of Ex. 26, a glass liner was filled with DMAB (0.95 g, 16.2 mmol), under a stream of N_2, inserted into the reactor, and the reactor was sealed. A solution of 0.5 mol% (0.08 mmol, 54 mg) **6e** in 5 mL of dried/N_2 saturated THF was added through the sampling valve via a gas-tight syringe and the valve was closed.

Example 30: Dehydrogenation of DMAB in THF with 6k at room temperature (Figure 3)

Following the procedure of Ex. 26, a glass liner was filled with DMAB (0.95 g, 16.2 mmol) and 0.5 mol% (0.08 mmol, 69 mg) **6k** under a stream of N_2, inserted into the reactor, and the reactor was sealed. 5 mL of dried/N_2 saturated THF was added through the sampling valve via a gas-tight syringe and the valve was closed.

Comparative Example 6: Dehydrogenation of DMAB in THF with catalyst 7 at room temperature (Figure 3)

Procedure as in Example 29. DMAB: 0.95 g (16.2 mmol); catalyst: 0.5 mol%, 0.08 mmol, 51 mg; THF: 5 mL.

Comparative Example 7: Dehydrogenation of DMAB in THF without catalyst at 42°C (Figure 7)

Procedure as in Comparative Example 6 without catalyst.

Examples 31-34, Comparative Example 8: Dehydrogenation of DMAB in THF at 42°C (Figure 4)

Following the procedure of Ex. 26.

Exp.	Catalyst			
31	**6k**	69 mg	0.08 mmol	0.5 mol%
32	**6e**	54 mg	0.08 mmol	0.5 mol%
33*	**6j**	60 mg	0.08 mmol	0.5 mol%
34#	**6g**	57 mg	0.08 mmol	0.5 mol%
Comp. Exp.	**Catalyst**			
8	**7**	54 mg	0.08 mmol	0.5 mol%

*) catalyst added dissolved in THF

#) DMAB added dissolved in THF

Example 35: Solvent-free dehydrogenation of DMAB at 42°C with catalyst 6e (Figure 5)

Following the procedure of Ex. 26. DMAB (51 mmol, 2.98 g) and **6e** (0.13 mol%, 0.06 mmol, 44 mg were reacted.

Comparative Example 9: Solvent-free dehydrogenation of DMAB at 42°C with catalyst 7 (Figure 5)

Following the procedure of Ex. 35. DMAB (51 mmol, 2.98 g) and **7** (0.13 mol%, 0.06 mmol, 40 mg) were reacted.

Comparative Example 10: Solvent-free dehydrogenation of DMAB at 42°C without catalyst (Figure 5)

Procedure as in Comparative Example 9 without catalyst.

Example 36: Dehydrogenation of DMAB in THF at room temperature with catalyst 6e under non-protective atmosphere (Figure 6)

Procedure as described in Ex. 29, but with standard THF and not under protective atmosphere.

Comparative Example 11: Dehydrogenation of DMAB in THF at room temperature without catalyst under non-protective atmosphere (Figure 6)

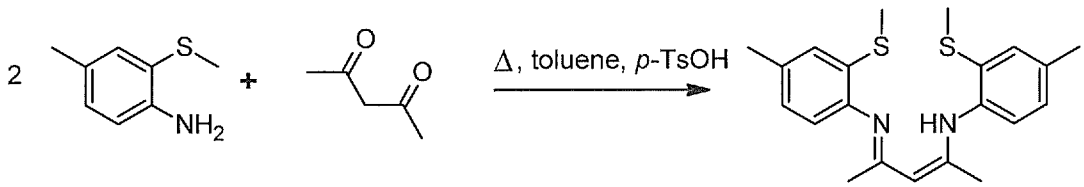
Procedure as described in Ex. 36, but without catalyst

Example 37: Dehydrogenation of DMAB in THF 42°C with catalyst 6e under addition of further aliquots of DMAB/THF solution (Figures 7a/7b)

Procedure as described in Ex. 28. To **6e** (0.5 mol%, 0.8 mmol, 54 mg) was added DMAB (0.95 g, 16 mmol) in THF (5 mL). Further aliquots of 1 mL of a total of 9.3 mL of DMAB (4.13 g) in THF (5 mL) were added.

Cycle	Effective DMAB conc. in solution	Remark
0	3.24 M	Reaction started as normal
1	1.26 M	1st aliquot added etc.
2	1.08 M	
3	0.94 M	
4	0.84 M	
5	0.75 M	
6	0.69 M	
7	0.63 M	
8	0.58 M	
9	0.54 M	
10	0.16 M	
11	0.82 M	Addition of higher conc. Stock solution next day
12	0.74 M	Rct. stirred
13	0.67 M	Rct. stirred, air purged (not inert)

Example 38: Synthesis of Ligand 9 (Scheme 10)



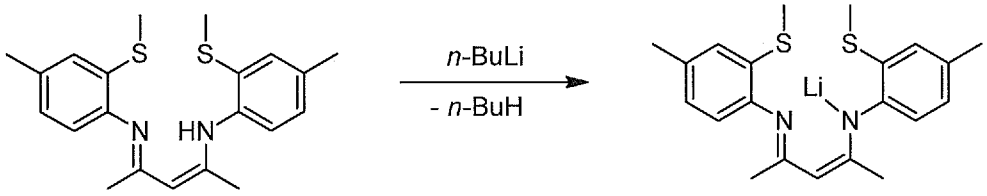
8 **9**

Scheme 10

Acetylacetone (0.96 g, 9.59 mmol) and p-toluenesulfonic acid monohydrate (2.00 g, 10.5 mmol) were added to a 3-neck round-bottom flask with a Dean-Stark apparatus connected. Degassed toluene (150 mL) and 4-methyl-2-(methylthio)aniline **8** (2.88 g,

18.67 mmol) were added to give a green solution, and the mixture refluxed at 150°C for 24 hours. The resulting yellow solution was cooled, and solvent removed. The resulting oil was taken up in dichloromethane (100 ml) and stirred with a solution of sodium carbonate (40 g in 100 ml H2O) for 30 minutes. The organic layer was separated and the aqueous layer extracted with dichloromethane (3 x 50 mL), the organic layers were combined, washed with brine, and dried over magnesium sulfate. The solvent was removed to give yellow oil. Recrystallization from methanol gave **9** as bright yellow powder (2.50 g, 70 %).

1H NMR (400 MHz, CDCl3) δ ppm: 1.89 (s, 6H, NCCH3), 2.32, 2.35 (2 s, 6H each, -SCH3, Ar-CH3), 4.92 (s, 1H, β-CH), 6.8-7.0 (m, 6H, Ar-CH), 12.42 (br s, 1H, NH).



9 **10**

Scheme 11

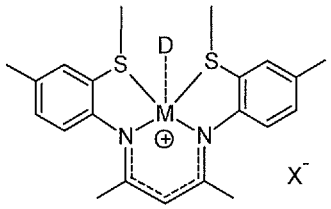
Example 39: Synthesis of Lithiated Ligand 10 (Scheme 11)

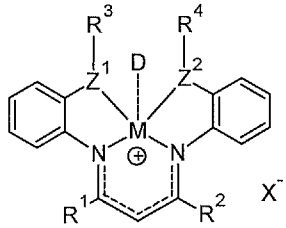
9 (1.00 g, 2.70 mmol) was added to a dried Schlenk. Dry degassed pentane was transferred via cannula, and the pale yellow mixture cooled on ice. *n*-BuLi (1.95 mL, 1.6M in hexanes) was added dropwise to give a bright yellow mixture. After stirring for 3 hours at room temperature, the solid precipitate was removed by filtration and the filtrate reduced in vacuum to give **10** as a bright yellow powder (0.28 g, 26%) which was reacted further without characterisation.

Examples for Metal Complexes

10 —a)→ **11a + 11b**
5a —b)→ **11c + 6f**
5a —c)→ **11d + 6f**
6a —d)→ **11e**
6a —e)→ **11f**
5a —f)→ **11g + 11h**

a) $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$, NaOTf, CH_2Cl_2
b) $\{[\eta^6\text{-}(p\text{-cymene})]RuCl\}_2Cl_2$, NaOTf, CH_2Cl_2
c) $\{[\eta^6\text{-}C_6(CH_3)_6]RuCl\}_2Cl_2$, NaOTf, CH_2Cl_2
d) $Na[(3,5\text{-}(CF_3)_2C_6H_3)_4B]$, CH_2Cl_2
e) $AgSbF_6$, CH_2Cl_2
f) $[(\eta^6\text{-}C_6H_6)OsCl]_2Cl_2$, NaOTf, CH_2Cl_2





11a: M = Ru; D = η^6–C_6H_6; X^- = OTf^-
11b: M = Ru; D = none; X^- = OTf^-

11c: M = Ru; D = η^6–(*p*-cymene); Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-
11d: M = Ru; D = η^6–$[C_6(CH_3)_6]$; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-
11e: M = Ru; D = η^6–C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; X^- = $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$
11f: M = Ru; D = η^6–C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; X^- = SbF_6^-
11g: M = Os; D = η^6–C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-
11h: M = Os; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

Scheme 12

Example 40: Synthesis of Ruthenium Complex 11a (Scheme 12)

10 (0.25 g, 0.66 mmol), $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$ (0.17g, 0.33 mmol) and sodium triflate (0.126g, 0.73 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to give a brown solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark red solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give the product as a dark red powder (0.20 g, 43 %). The NMR for this complex shows two species, one containing the coordinated benzene ring (**11a**), and one where benzene has been lost (**11b**). Percentage yield based on complex **11a**. Each of the species occurs in different stereoisomers yielding a highly complex ^1H NMR spectrum. ^1H NMR (400 MHz, CD_2Cl_2) δ ppm: 2.05-2.56 (m, CH_3), 4.87-5.27 (m, C_6H_6), 5.95 (s, β-C*H*), 6.97-7.35 (m, Ar-*H*). ^{19}F NMR (376 MHz, CD_2Cl_2) δ ppm: -78.7 (OTf).

Example 41: Synthesis of Ruthenium Complex 11c (Scheme 12)

5a (0.40 g, 1.19 mmol), $\{[\eta^6\text{-}(C_6(CH_3)_6)]RuCl\}_2Cl_2$ (0.34g, 0.57 mmol) and sodium triflate (0.23 g, 1.32 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to give a brown solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark red solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give the product as a dark red powder (0.50 g, 64 %). The NMR for this complex shows two species, one containing the coordinated *p*-cymene (**11c**), and one where *p*-cymene has been lost (**6f**). Percentage yield based on complex **11c**.

^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 1.17-1.22 (m, 1 H, *p*-cymene-C*H*), 1.89 (s, 3 H, *p*-cymene-CH_3), 2.09 & 2.11 (2 s, 3H, SCH_3), 2.20 (s, 6H, NCCH_3), 2.36 (s, 3H, SCH_3), 2.55 & 2.56 (s, 6H, *p*-cymene-CH_3), 4.52-4.99 (m, 4 H, *p*-cymene-Ar-*H*), 6.27 & 6.29 (2 s, 1H, β-C*H*), 7.09-7.11 (m, 2H, Ar-*H*). ^{19}F NMR (376 MHz, CD_2Cl_2) δ ppm: -78.8 (OTf).

Example 42: Synthesis of Ruthenium Complex 11d (Scheme 12)

5a (0.21 g, 0.56 mmol), $\{[\eta^6\text{-}(p\text{-cymene})]RuCl\}_2Cl_2$ (0.20 g, 0.30 mmol) and sodium triflate (0.11 g, 0.66 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to give a brown solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark red solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give the product as a dark red powder (0.50 g, 64 %). The NMR for this complex shows two species, one containing the coordinated hexamethylbenzene ring (**11c**), and one where hexamethylbenzene has been lost (**6f**). Percentage yield based on complex **11c**. Each of the species occurs in different stereoismoers yielding a highly complex ^{1}H NMR spectrum.

Example 43: Synthesis of Ruthenium Complex 11e (Scheme 12)

A solution of **6a** (0.20g, 0.29 mmol) in dry degassed dichloromethane (10 mL) was added to a solution of $Na[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]$ (0.36 g, 0.41 mmol) in dry degassed dichloromethane (10 mL) in a Schlenk. The resulting dark red brown solution which was stirred for 18 hours under N_2 at room temperature. The solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give **11e** as a green powder (0.35 g, 94 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 2.12 (s, 6H, NCC*H*$_3$), 2.22-2.54 (m (different stereoisomers), 6H, SC*H*$_3$), 5.20 (s, 6H, C_6H_6), 6.29 (s, 1H, β-C*H*), 7.30-7.48 (m, 8H, Ar-*H*), 7.59 & 7.76 (2 s br, 12H, BARF-*H*). ^{19}F NMR (282 MHz, CD_2Cl_2) δ ppm: -62.77 (BAr^F_4).

Example 44: Synthesis of Ruthenium Complex 11f (Scheme 12)

6a (0.20g, 0.29 mmol) and silver hexafluoroantimonate (0.14 g, 0.41 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to give a dark red brown solution which was stirred for 18 hours under N_2 at room temperature and under protection from light. The solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give **11f** as a green powder (0.15 g, 68 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 2.21 & 2.22 (2 s (different stereoisomers), 6H, NCC*H*$_3$), 2.55 (s, 6H, SC*H*$_3$), 5.23 (s, 6H, C_6H_6), 6.42 (s, 1H, β-C*H*), 7.35-7.50 (m, 8H, Ar-*H*).

Example 45: Synthesis of Ruthenium Complex 11g (Scheme 12)

5a (0.21 g, 0.60 mmol), $[(\eta^6\text{-}C_6H_6)OsCl]_2Cl_2$ (0.20 g, 0.29 mmol) and sodium triflate (0.13 g, 0.76 mmol) were added to a dry Schlenk. Dry degassed dichloromethane (10 mL) was transferred via cannula to give a brown solution which was stirred for 18 hours under N_2 at room temperature. The resulting dark red solution was filtered through Celite, washed with dry dichloromethane and the solvent removed in vaccuo. The residue was washed with dry pentane, which was decanted and the solid dried to give the product as a dark brown powder (0.26 g, 56 %). Crystals suitable for x-ray were grown by slow diffusion (THF). The NMR for this complex shows two species, one containing the coordinated benzene ring (**11g**), and one where benzene has been lost (**11h**). Percentage yield based on complex **11g**.

^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm: 1.89, 2.28, 2.30, 2.36 (4 s (different stereoisomers), 6H, SC*H*$_3$), 2.53 (s, 6H, NCC*H*$_3$), 5.85 (s, 6H, C_6H_6), 6.04 (s, 1H, β-C*H*), 6.76-7.42 (m, 8H, Ar-*H*). ^{19}F NMR (376 MHz, CD_2Cl_2) δ ppm: -78.8 (OTf).

Examples for Dehydrogenation Reactions

Examples 46-50, Comparative Example 8: Dehydrogenation of DMAB in THF at 42°C (Figure 9)

Following the procedure of Exp. 26.

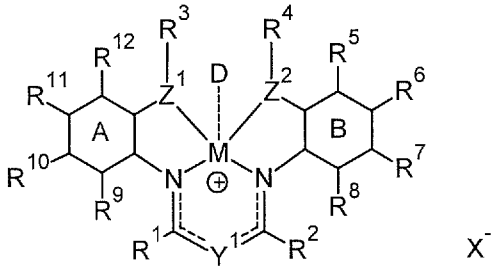
Exp.	Catalyst			
46#	**11a**	57 mg	0.08 mmol	0.5 mol%
47#	**11c**	59 mg	0.08 mmol	0.5 mol%
48#	**11d**	61 mg	0.08 mmol	0.5 mol%
49#	**11e**	104 mg	0.08 mmol	0.5 mol%
50#	**11f**	104 mg	0.08 mmol	0.5 mol%
Comp. Exp.	**Catalyst**			
8	**7**	54 mg	0.08 mmol	0.5 mol%

#) DMAB added dissolved in THF

Various modifications and variations of the described aspects of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes of carrying out the invention which are obvious to those skilled in the relevant fields are intended to be within the scope of the following claims.

CLAIMS

1. A process for the production of hydrogen comprising contacting at least one complex of formula (I),



(I)

wherein:

X^- is an anion;

M is a metal selected from Ru, Os, Fe, Co and Ni;

D is optionally present and is one or more monodentate or multidentate donor ligands;

Y^1 is selected from CR^{13}, B and N;

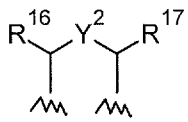
Z^1 and Z^2 are each independently selected from =N, =P, NR^{14}, PR^{15}, O, S and Se; or

Z^2 is a direct bond between carbocyclic ring B and substituent R^4;

each of A and B is independently a saturated, unsaturated or partially unsaturated carbocyclic hydrocarbon ring;

R^3 and R^4 are each independently selected from H, C_{1-6}-alkyl, aryl and C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support; or

R^3 and R^4 together form the following moiety:



Y^2 is a direct single bond or double bond, or is CR^{18};

R^1, R^2, R^{5-13} and R^{16-18} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, $NR^{19}R^{20}$ and a linker group optionally attached to a solid support;

or two or more of said R^{1-13} and R^{16-18} groups are linked, together with the carbons to which they are attached, to form a saturated or unsaturated hydrocarbon group;

R^{14}, R^{15}, R^{19} and R^{20} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support;

with at least one substrate of formula (II)

$$R^{21}R^{22}NH\text{-}BHR^{23}R^{24}$$

(II)

wherein R^{21} to R^{24} are each independently selected from H, C_{1-6}-alkyl, fluoro-substituted C_{1-6}-alkyl, C_{6-14}-aryl and C_{6-14}-aralkyl, or any two of R^{21}, R^{22}, R^{23} and R^{24} are linked to form a C_{3-10}-alkylene group or C_{3-10}-alkenylene group, which together with the nitrogen and/or boron atoms to which they are attached, forms a cyclic group;

or a substrate comprising two, three or four substrates of formula (II) linked via one or more bridging groups so as to form a dimeric, trimeric or tetrameric species, and wherein the bridging group is selected from straight or branched C_{1-6}-alkylene optionally substituted by one or more fluoro groups; boron; C_{6-14}-aryl; and C_{6-14}-aralkyl;

or a substrate comprising two, three or four substrates of formula (II) which are joined so as to form a fused cyclic dimeric, trimeric or tetrameric species.

2. A process according to claim 1 wherein R^{23} and R^{24} are both H, one of R^{21} and R^{22} is H and the other is selected from H, CF_3, methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl, tert-butyl, sec-butyl, phenyl and benzyl.

3. A process according to claim 1 wherein R^{23} and R^{24} are both H, and R^{21} and R^{22} are each independently selected from H, CF_3, methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl, tert-butyl, sec-butyl, phenyl and benzyl, or R^{21} and R^{22} are linked to form a C_4-alkylene group, which together with the nitrogen atom to which they are attached, forms a cyclic group.

4. A process according to claim 1 wherein the substrate of formula (II) is selected from ammonia borane, methylamine borane, dimethylamine borane, di-isopropylamine

borane, isopropylamine borane, tert-butylamine borane, isobutylamine borane, phenylamine borane and pyrrolidine borane, and mixtures thereof.

5. A process according to any preceding claim wherein the substrate of formula (II) is ammonia borane (H_3B-NH_3).

6. A process according to any preceding claim wherein X^- is selected from OTf^-, BF_4^-, PF_6^-, BPh_4^- and $BArF^-$ ($B((3,5\text{-}CF_3)_2C_6H_3)_4^-$), more preferably, OTf^-.

7. A process according to any preceding claim wherein M is selected from Ru, Ni and Co.

8. A process according to any preceding claim wherein R^5 to R^{18} are each independently selected from H, methyl, CF_3 and isopropyl.

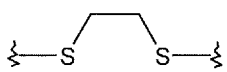
9. A process according to any preceding claim wherein R^3 and R^4 are both independently $C_{1\text{-}6}$-alkyl, more preferably, Me.

10. A process according to any preceding claim wherein Y_1 is CR^{13}, more preferably CH.

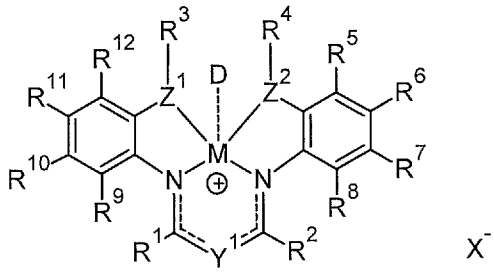
11. A process according to any preceding claim wherein A and B are both phenyl groups.

12. A process according to any preceding claim wherein Z^1R^3 and Z^2R^4 are each independently S-$C_{1\text{-}6}$-alkyl, more preferably Z^1R^3 and Z^2R^4 are each independently selected from SCH_3 and SCH_2CH_3.

13. A process according to any one of claims 1 to 11 wherein Z^1R^3 and Z^2R^4 together form the following moiety:



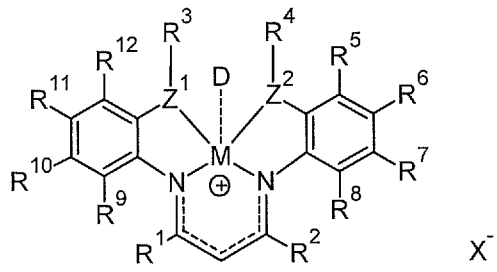
14. A process according to claim 1 wherein the compound of formula (I) is a compound of formula (V):



(V)

wherein R^1-R^{12}, D, M, Z^1, Z^2, Y^1 and X^- are as defined in claim 1.

15. A process according to claim 1 wherein the compound of formula (I) is a compound of formula (Va):



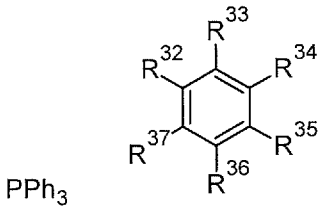
(Va)

wherein:

X^- is an anion selected from Cl^-, Br^-, PF_6^-, TfO^-;

M is selected from Ru and Ni;

D is optional and is selected from (VI) and (VII),



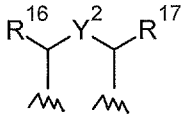
(VI)

(VII)

Z^1 and Z^2 are each independently selected from NR^{14}, PR^{15}, O and S; or Z^2 is a direct bond to R^4;

R^3 and R^4 are each independently selected from H, $C_{1\text{-}6}$-alkyl, aryl and $C_{1\text{-}6}$-haloalkyl, and a linker group optionally attached to a solid support; or

R^3 and R^4 together form the following moiety:



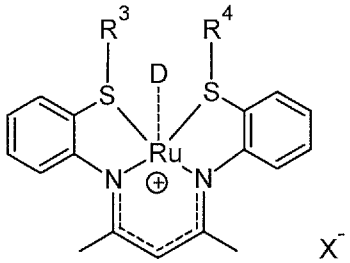
Y^2 is a direct single bond or double bond, or is CR^{18};

R^1, R^2, R^{5-13} and R^{16-18} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, $NR^{19}R^{20}$ and a linker group optionally attached to a solid support;

or two or more of said R^{1-13} and R^{16-18} groups are linked, together with the carbons to which they are attached, to form a saturated or unsaturated hydrocarbon group; and

R^{14}, R^{15}, R^{19}, R^{20} and R^{32-36} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support.

16. A process according to claim 1 wherein the compound of formula (I) is a compound of formula (VIII):



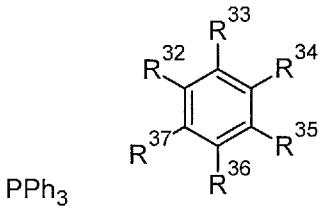
(VIII)

wherein R^3, R^4, D and X^- are as defined in claim 1.

17. A process according to claim 1 wherein:

X^- is an anion selected from Cl^- and TfO^-;

D is optional and is selected from (VI) and (VII),



(VI) (VII)

R^3 and R^4 are each independently selected from H, C_{1-6}-alkyl, aryl and C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support.

18. A compound according to any preceding claim wherein:

(i) D is η^6-C_6H_6, and X^- is Cl^-;

(ii) D is η^6-C_6H_6, and X^- is OTf^-;

(iii) D is absent, and X^- is Cl^-;

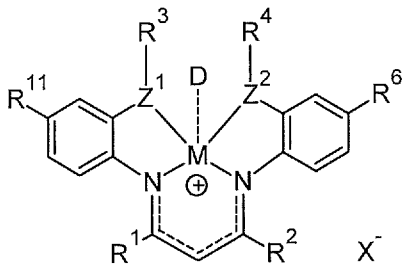
(iv) D is absent, and X^- is OTf^-;

(v) D is PPh_3, and X^- is Cl^-;

(vi) D is PPh_3, and X^- is OTf^-; or

(vii) D is absent, and X^- is Br^-.

19. A process according to any preceding claim wherein the compound of formula (I) is a compound selected from the following:



(IXa)

Compound 6a: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6b: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6c: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6d: M = Ru; D = η^6-C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6f: M = Ru; D = none; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6g: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6h: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6i: M = Ru; D = η^6-C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6j: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6k: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6l: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = Br^-

Compound 6m: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = PF_6^-

Compound 6n: M = Ni; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^3 and R^4 together = CH_2CH_2; $R^{6,11}$ = H; X^- = PF_6^-

Compound 6q: M = Ru; D = PPh_3; Z^{1-2} = S; $R^{1-2,6,11}$ = H; R^{3-4} = CH_3; X^- = ^-OTf

Compound 6r: M = Ru; D = PPh_3; Z^{1-2} = S; $R^{1-2,6,11}$ = H; R^{3-4} = CH_3; X^- = Cl^-

Compound 11a: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; $R^{1-4,6,11}$ = CH_3; X^- = ^-OTf

Compound 11b: M = Ru; D = none; Z^{1-2} = S; $R^{1-4,6,11}$ = CH_3; X^- = ^-OTf

Compound 11c: M = Ru; D = η^6-(*p*-cymene); Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 11d: M = Ru; D = η^6-[$C_6(CH_3)_6$]; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

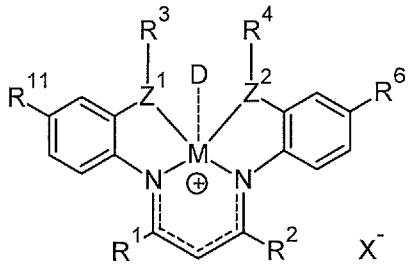
Compound 11e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = [(3,5-$(CF_3)_2C_6H_3)_4B]^-$

Compound 11f: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = SbF_6^-

Compound 11g: M = Os; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 11h: M = Os; D = none; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

20. A process according to any preceding claim wherein the compound of formula (I) is a compound of formula (VII) selected from the following:



(IXa)

Compound 6e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6f: M = Ru; D = none; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6g: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6h: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 6j: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = Cl^-

Compound 6k: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 11a: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; $R^{1-4,6,11}$ = CH_3; X^- = ^-OTf

Compound 11b: M = Ru; D = none; Z^{1-2} = S; $R^{1-4,6,11}$ = CH_3; X^- = ^-OTf

Compound 11c: M = Ru; D = η^6-(*p*-cymene); Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

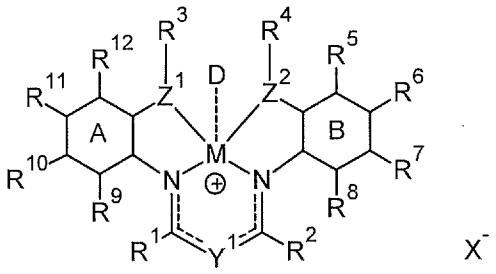
Compound 11d: M = Ru; D = η^6-[$C_6(CH_3)_6$]; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 11e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = [(3,5-$(CF_3)_2C_6H_3)_4B]^-$

Compound 11f: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = SbF_6^-

21. A hydrogen generation system comprising:

(a) at least one complex of formula (I)



(I)

wherein:

X^- is an anion;

M is a metal selected from Ru, Os, Fe, Co and Ni;

D is optionally present and is one or more monodentate or multidentate donor ligands;

Y^1 is selected from CR^{13}, B and N;

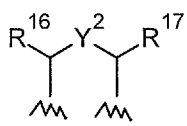
Z^1 and Z^2 are each independently selected from =N, =P, NR^{14}, PR^{15}, O, S and Se; or

Z^2 is a direct bond between carbocyclic ring B and substituent R^4;

each of A and B is independently a saturated, unsaturated or partially unsaturated carbocyclic hydrocarbon ring;

R^3 and R^4 are each independently selected from H, C_{1-6}-alkyl, aryl and C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support; or

R^3 and R^4 together form the following moiety:



Y^2 is a direct single bond or double bond, or is CR^{18};

R^1, R^2, R^{5-13} and R^{16-18} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, $NR^{19}R^{20}$ and a linker group optionally attached to a solid support;
or two or more of said R^{1-13} and R^{16-18} groups are linked, together with the carbons to which they are attached, to form a saturated or unsaturated hydrocarbon group;

R^{14}, R^{15}, R^{19} and R^{20} are each independently selected from H, C_{1-6}-alkyl, C_{2-6}-alkenyl, C_{2-6}-alkynyl, aryl, C_{1-6}-haloalkyl, and a linker group optionally attached to a solid support;

(b) at least one substrate of formula (II)

$$R^{21}R^{22}NH\text{-}BHR^{23}R^{24}$$

(II)

wherein R^{21} to R^{24} are each independently selected from H, C_{1-6}-alkyl, fluoro-substituted C_{1-6}-alkyl, C_{6-14}-aryl and C_{6-14}-aralkyl, or any two of R^{21}, R^{22}, R^{23} and R^{24} are linked to form a C_{3-10}-alkylene group or C_{3-10}-alkenylene group, which together with the nitrogen and/or boron atoms to which they are attached, forms a cyclic group;

or a substrate comprising two, three or four substrates of formula (II) linked via one or more bridging groups so as to form a dimeric, trimeric or tetrameric species, and wherein the bridging group is selected from straight or branched C_{1-6}-alkylene optionally substituted by one or more fluoro groups, boron, C_{6-14}-aryl and C_{6-14}-aralkyl;

or a substrate comprising two, three or four substrates of formula (II) which are joined so as to form a fused cyclic dimeric, trimeric or tetrameric species; and

(c) optionally, a solvent.

22. A hydrogen generation system according to claim 21, comprising a first compartment comprising the at least one complex of formula (I), a second compartment comprising the at least one substrate of formula (II), and a means for combining the contents of the first compartment with the contents of the second compartment such that when the contents are combined, hydrogen is generated.

23. A hydrogen generation system according to claim 22, which further comprises at least one flow controller to control a flow rate of the at least one complex of formula (I) or the at least one substrate of formula (II).

24. A hydrogen generation system according to any one of claims 21 to 23 wherein said system is connected to a proton exchange membrane fuel cell (PEMFC), or any other system requiring a supply of hydrogen.

25. Use of at least one complex of formula (I) as defined in claim 1 in a fuel cell.

26. A fuel cell comprising at least one complex of formula (I) as defined in claim 1.

27. A method of thermolytically dehydrogenating a substrate of formula (II) as defined in claim 1, said method comprising contacting at least one substrate of formula (II) as defined in claim 1 with a complex of formula (I) as defined in claim 1 in the presence of a solvent.

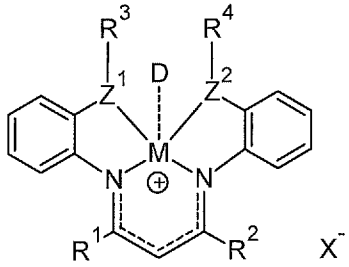
28. Use of at least one complex of formula (I) as defined in claim 1 in a method of thermolytically dehydrogenating a substrate of formula (II) as defined in claim 1.

29. Use of at least one complex of formula (I) as defined in claim 1 in a method of producing hydrogen.

30. A method of using a hydrogen generation system according to any one of claims 21 to 23 which comprises modulating the hydrogen pressure in said system so as to modulate activity of the at least one complex of formula (I).

31. A process, method, use or hydrogenation system, substantially as described herein, with reference to the accompanying figures.

32. A complex of formula (VII) selected from the following:



(IXa)

Compound 6a: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Cl^-

Compound 6b: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; X^- = Cl^-

Compound 6c: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4} = CH_2CH_3; X^- = Cl^-

Compound 6d: M = Ru; D = η^6-C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; X^- = Cl^-

Compound 6e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

Compound 6f: M = Ru; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

Compound 6g: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; X^- = OTf^-

Compound 6h: M = Ru; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^{3-4}= CH_2CH_3; X^- = OTf^-

Compound 6i: M = Ru; D = η^6-C_6H_6; Z^{1-2} = O; R^{1-4} = CH_3; X^- = OTf^-

Compound 6j: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Cl^-

Compound 6k: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-4} = CH_3; X^- = OTf^-

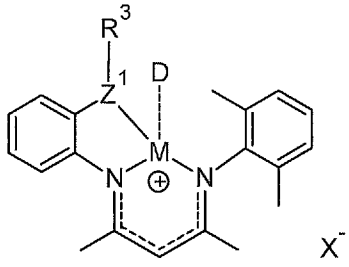
Compound 6l: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = Br^-

Compound 6m: M = Ni; D = none; Z^{1-2} = S; R^{1-4} = CH_3; X^- = PF_6^-

Compound 6n: M = Ni; D = none; Z^{1-2} = S; R^{1-2} = CH_3; R^3 and R^4 together = CH_2CH_2; X^- = PF_6^-

Compound 6q: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-2} = H; R^{3-4} = CH_3; X^- = OTf^-

Compound 6r: M = Ru; D = PPh_3; Z^{1-2} = S; R^{1-2} = H; R^{3-4} = CH_3; X^- = Cl^-



(IXb)

Compound 6o: M = Ru; D = η^6-C_6H_6; Z^1 = S; R^3 = CH_3; X^- = Cl^-

Compound 6p: M = Ru; D = η^6-C_6H_6; Z^1 = S; R^3 = CH_3; X^- = OTf^-

Compound 11a: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; $R^{1-4,6,11}$ = CH_3; X^- = ^-OTf

Compound 11b: M = Ru; D = none; Z^{1-2} = S; $R^{1-4,6,11}$ = CH_3; X^- = ^-OTf

Compound 11c: M = Ru; D = η^6-(*p*-cymene); Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = ^-OTf

Compound 11d: M = Ru; D = η^6-[$C_6(CH_3)_6$]; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = $^-$OTf

Compound 11e: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = [(3,5-$(CF_3)_2C_6H_3)_4B]^-$

Compound 11f: M = Ru; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = SbF_6^-

Compound 11g: M = Os; D = η^6-C_6H_6; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = $^-$OTf

Compound 11h: M = Os; D = none; Z^{1-2} = S; R^{1-4} = CH_3; $R^{6,11}$ = H; X^- = $^-$OTf

Figure 1

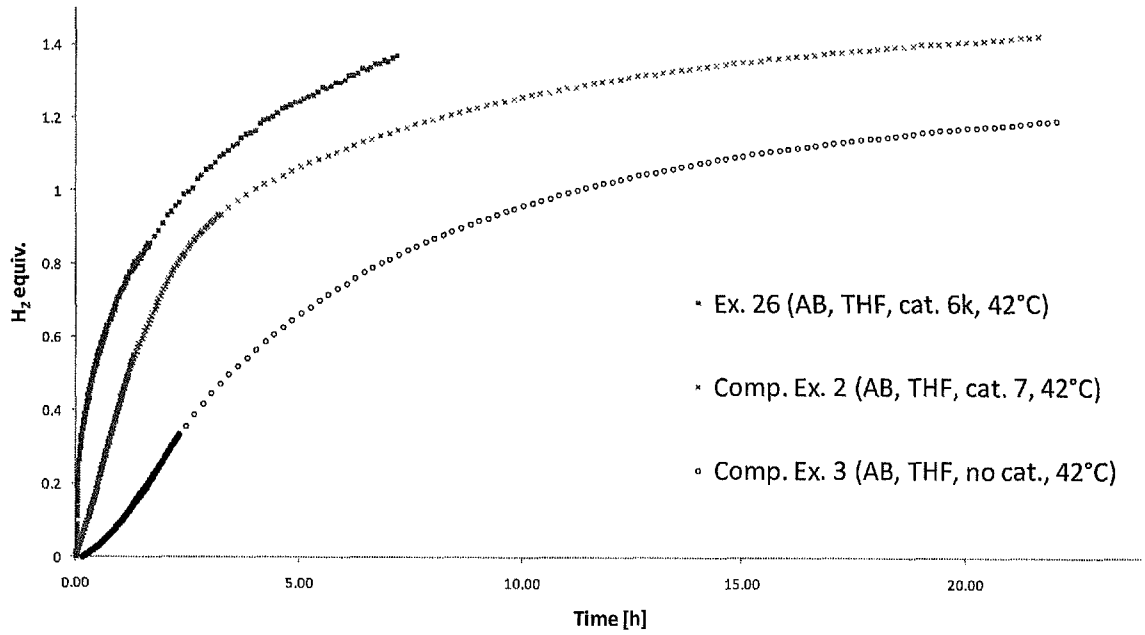


Figure 2

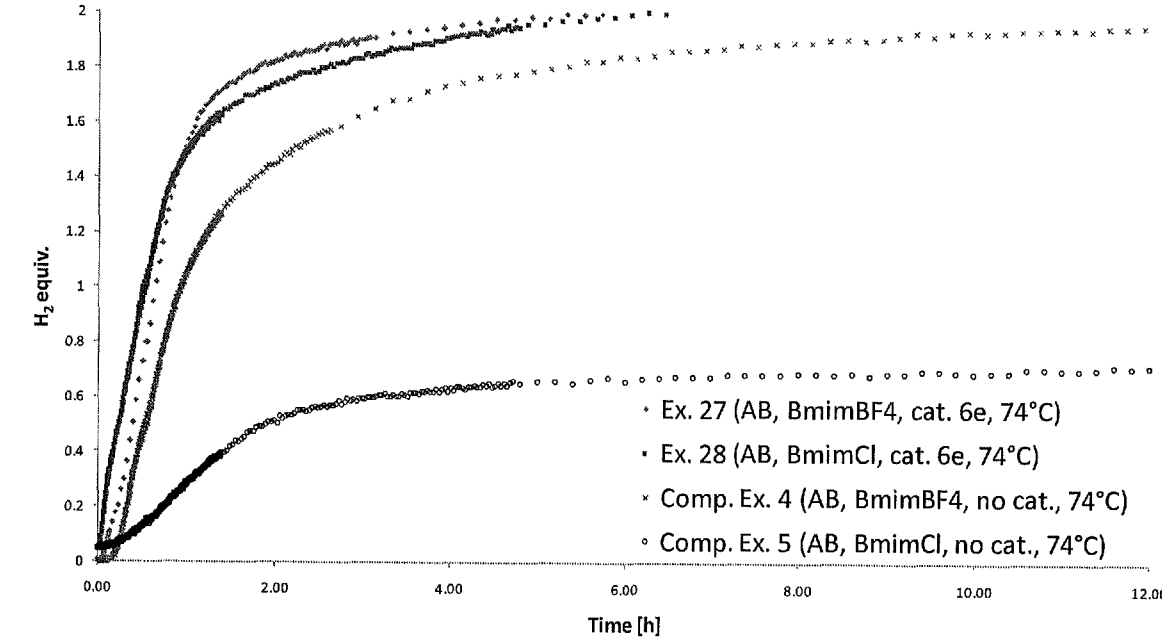


Figure 3

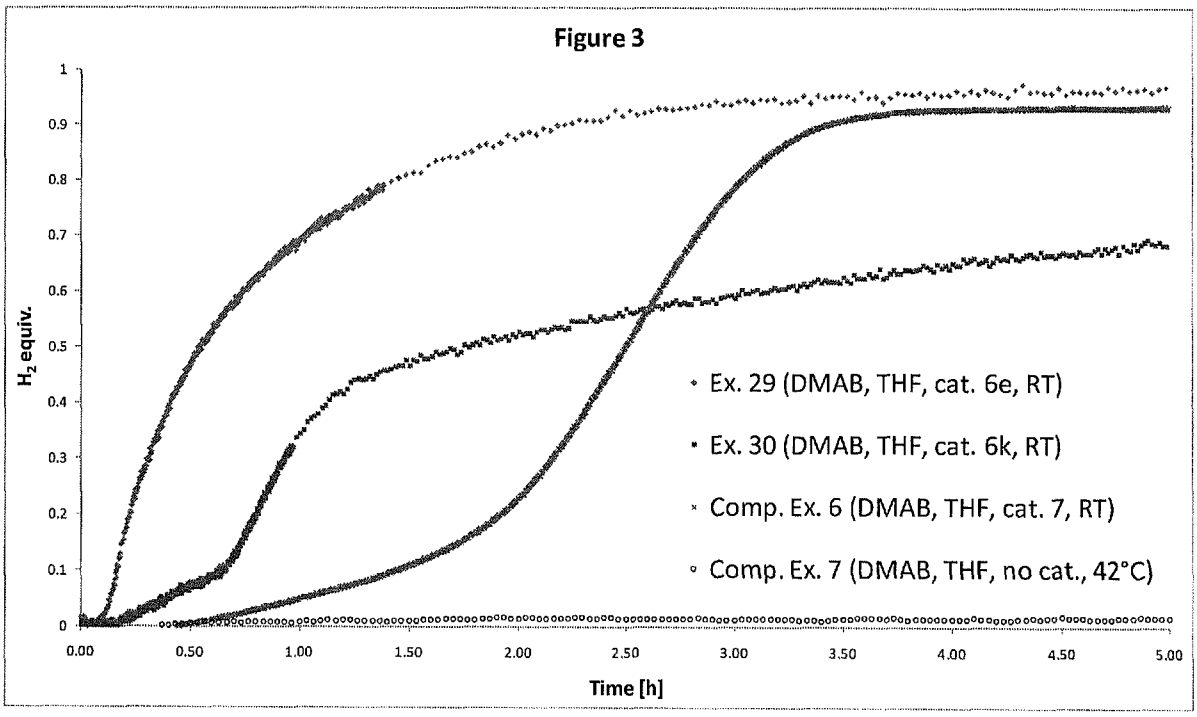


Figure 4

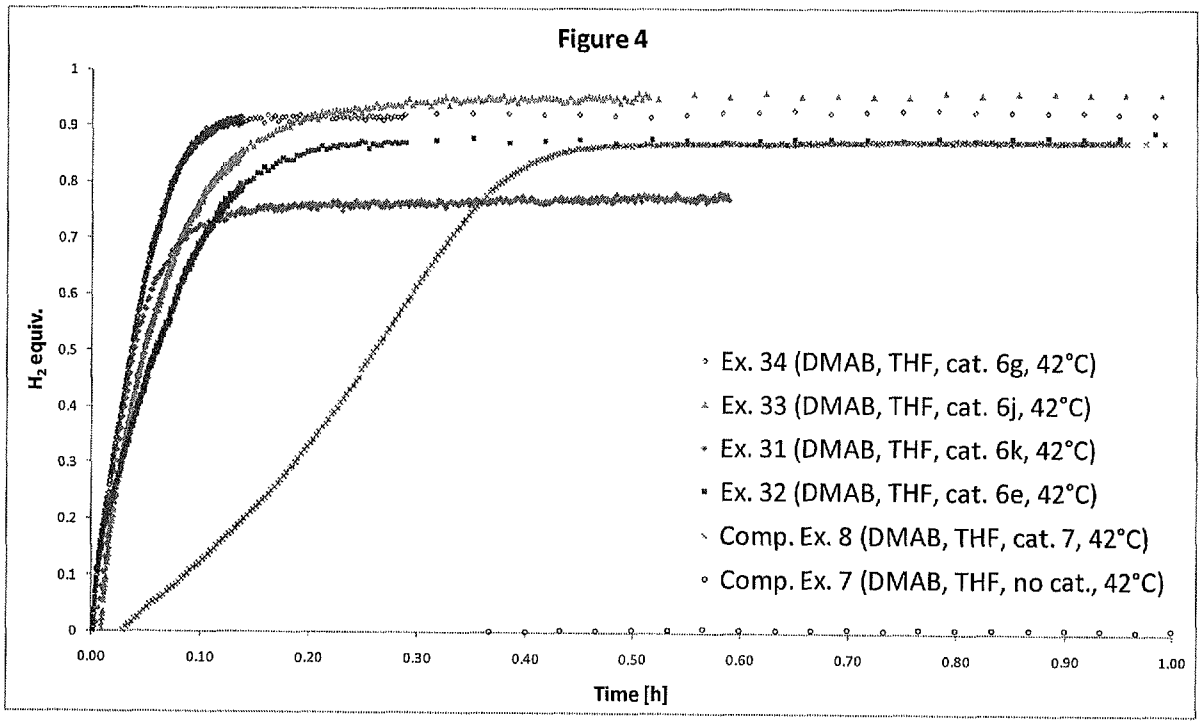


Figure 5

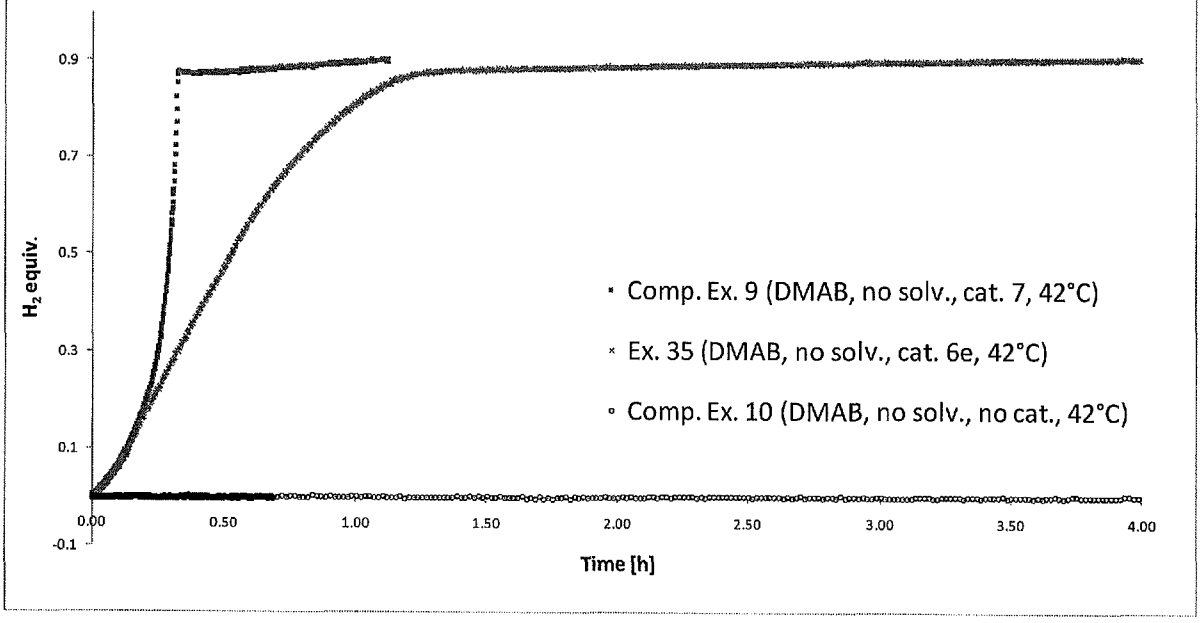


Figure 6

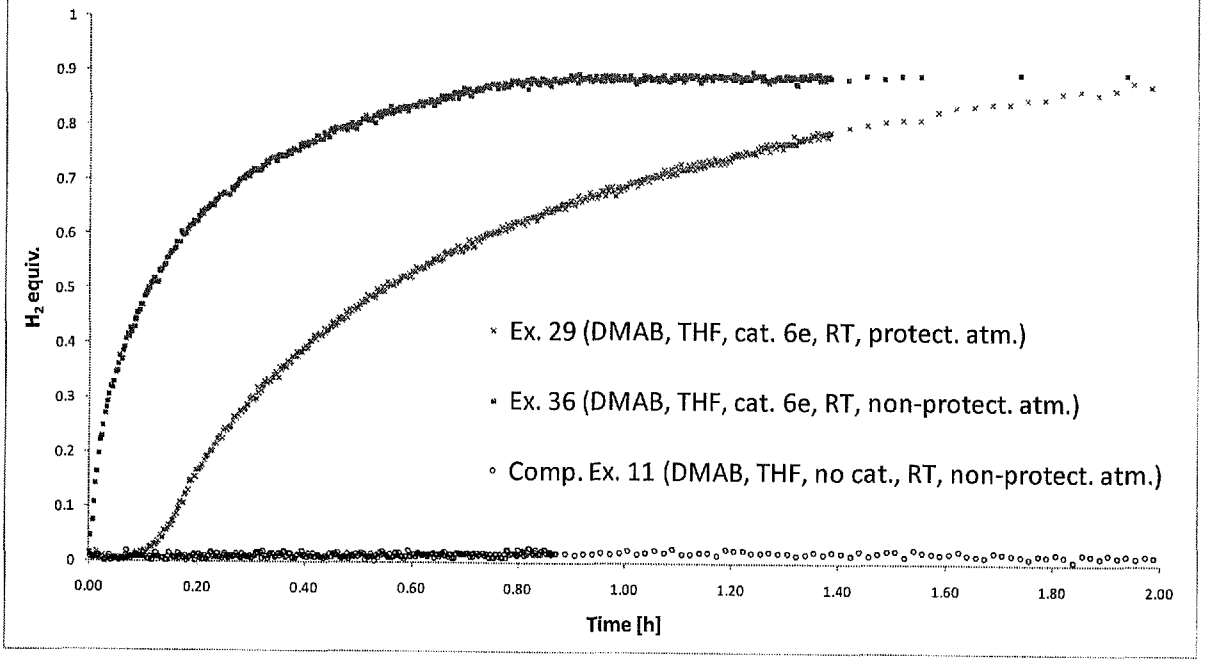


Figure 7a

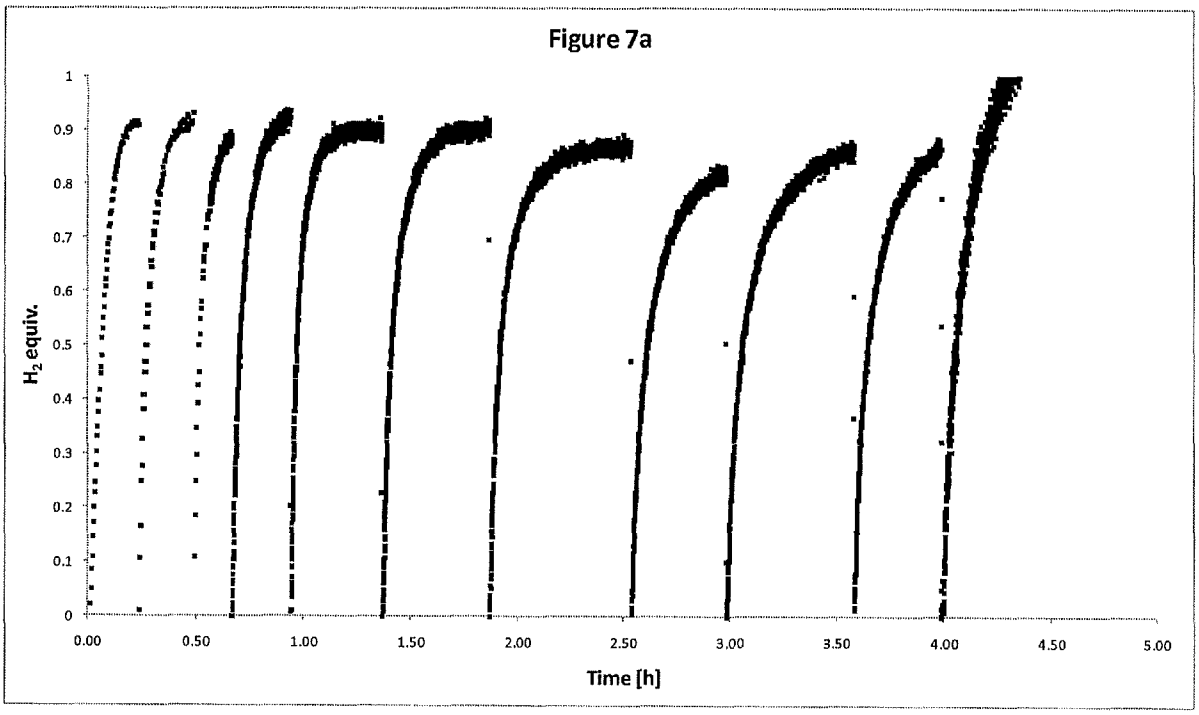
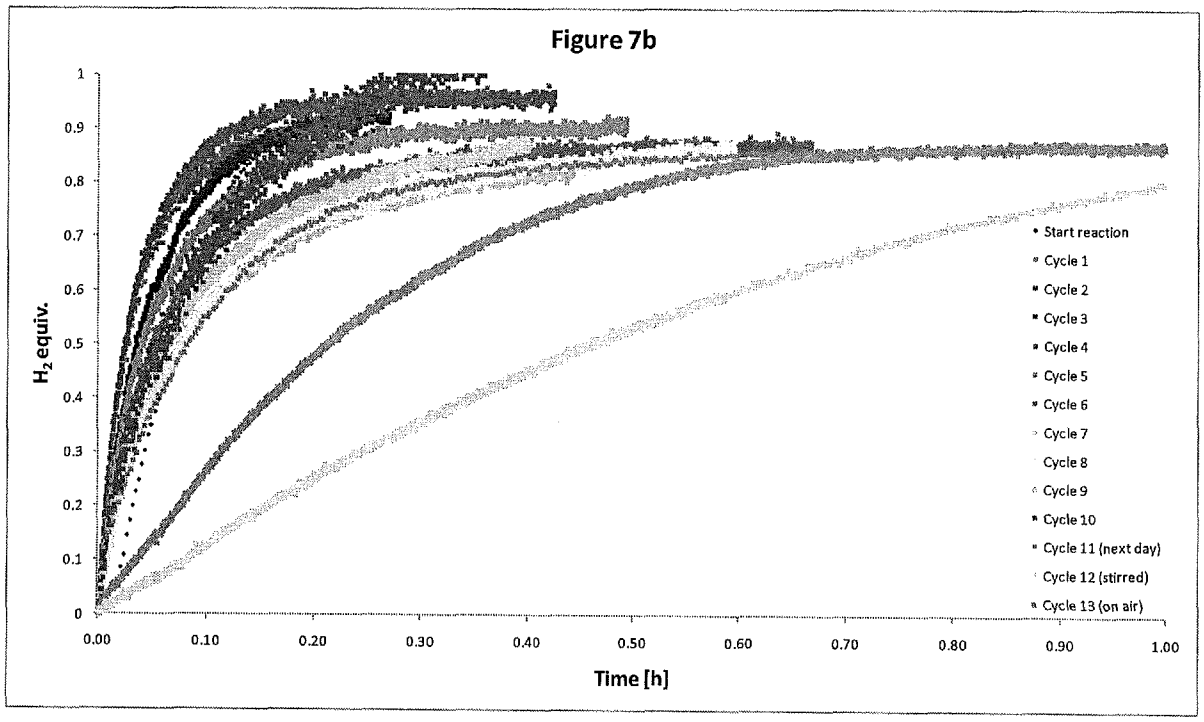


Figure 7b



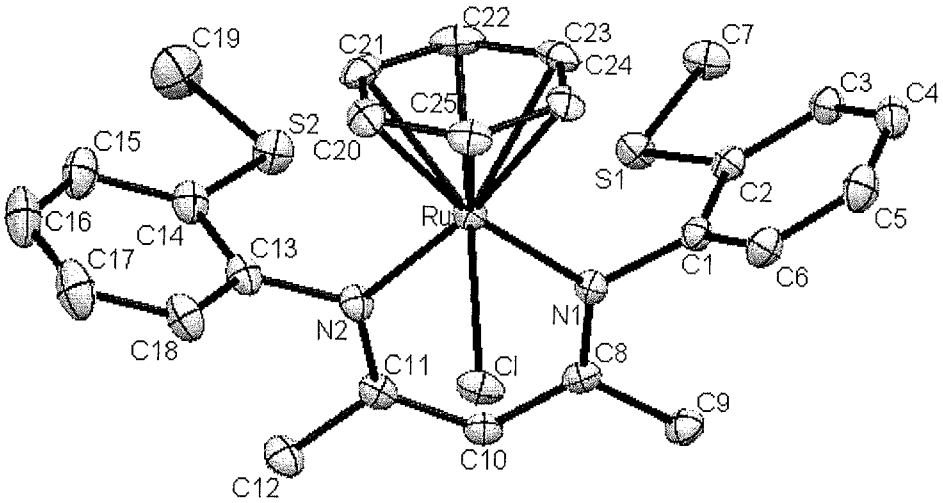

C19
C21
C22
C23
C24
C7
C3
C4
C25
S2
C20
C15
S1
C2
C16
C14
Ru
C5
C17
C13
C1
C6
N2
N1
C18
C11
Cl
C8
C9
C10
C12

Figure 8

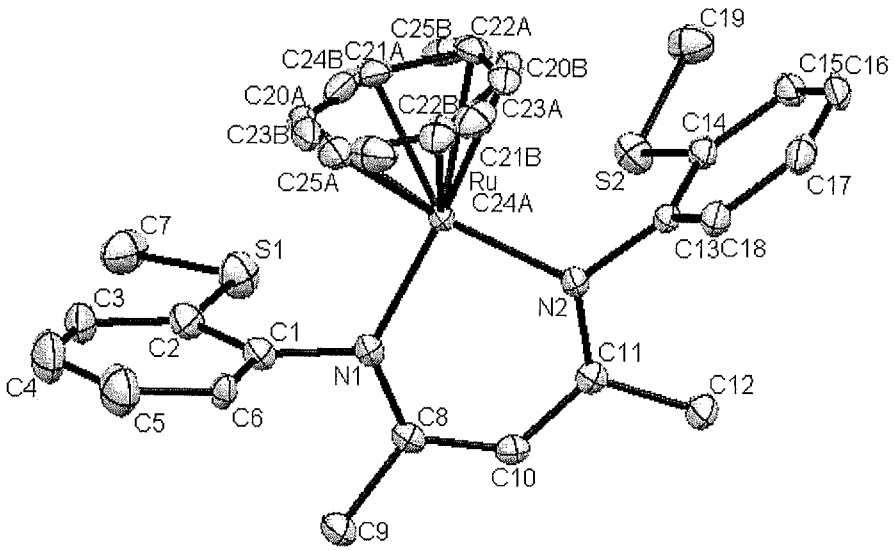

C25B
C22A
C19
C24B
C21A
C20B
C15C16
C20A
C22B
C23A
C14
C23B
C21B
S2
C17
C25A
Ru
C24A
C7
S1
C13C18
C3
N2
C1
C2
C11
N1
C4
C12
C5
C6
C8
C10
C9

Figure 9

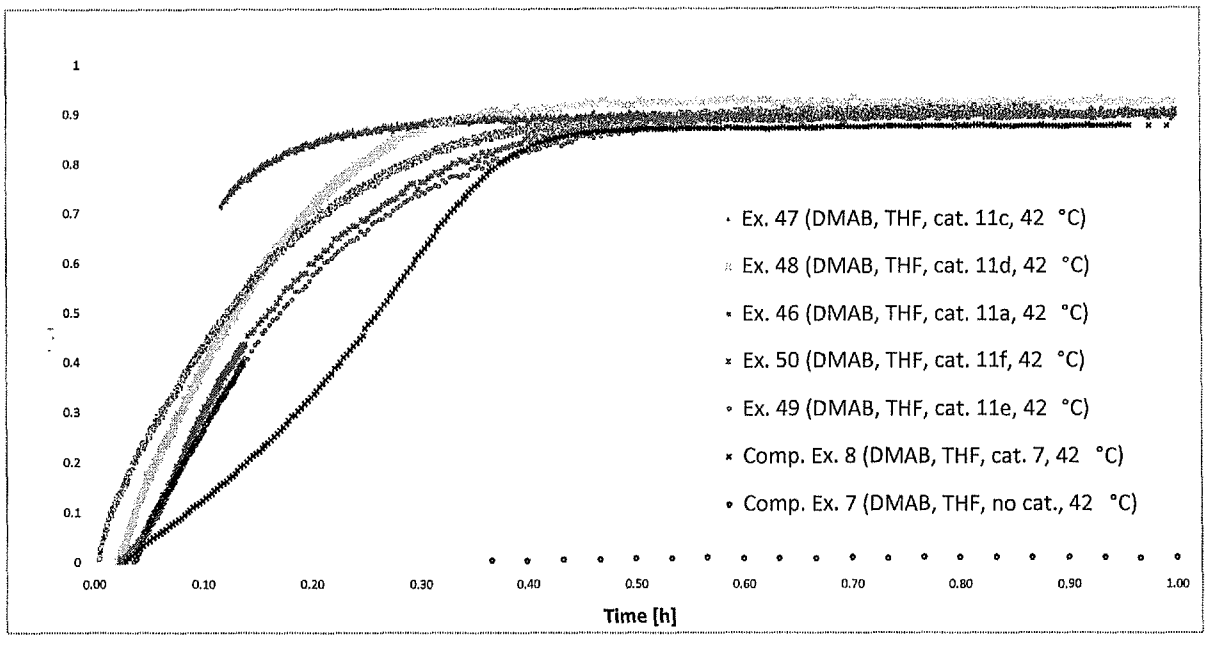

1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
Time [h]
Ex. 47 (DMAB, THF, cat. 11c, 42 °C)
Ex. 48 (DMAB, THF, cat. 11d, 42 °C)
Ex. 46 (DMAB, THF, cat. 11a, 42 °C)
Ex. 50 (DMAB, THF, cat. 11f, 42 °C)
Ex. 49 (DMAB, THF, cat. 11e, 42 °C)
Comp. Ex. 8 (DMAB, THF, cat. 7, 42 °C)
Comp. Ex. 7 (DMAB, THF, no cat., 42 °C)

Figure 10