CATALYSTS AND PROCESS FOR HYDROGEN STORAGE BASED ON FORMATE-BICARBONATE EQUILIBRIUM IN AQUEOUS MEDIUM

The invention relates to the use of an isolated or non-isolated (*in situ* generated) catalyst comprising an **M** central metal and at least one strong sigma-donor ligand selected from **NHC** N-heterocyclic carbene ligands and **Pws** water-soluble phosphine ligands in a process for storing hydrogen gas and/or in a process for releasing hydrogen gas, wherein the storage of hydrogen gas and the release of hydrogen gas are based on a formate-bicarbonate equilibrium, wherein **M** is a metal selected from non-platinum transition metals, p-field metals and f-field metals, **NHC** is an N-heterocyclic carbene ligand, **Pws** is a water-soluble phosphine ligand. The invention further relates to a process for a hydrogen gas storage system and a hydrogen gas release system, wherein the storage of hydrogen gas is carried out by hydrogenation of bicarbonates in the presence of the catalyst as described in the specification in an aqueous medium, and the release of hydrogen gas free of CO_x by-products is carried out by decomposition of formates in the presence of the catalyst as described in the specification in an aqueous medium; and wherein preferably the storage of hydrogen gas and the release of hydrogen gas are carried out with the same catalyst in a single system.

STATE OF THE ART

The demand for hydrogen storage is growing. Hydrogen, as a raw material, fuel and energy carrier, can play an important role in achieving decarbonization goals. In addition, hydrogen can also be considered a flexible energy storage option in the long term: various alternative energy sources (solar, geothermal, wind, biomass, etc.) can be used to produce hydrogen, the storage and subsequent release of which can balance out fluctuations in alternative energy production.

However, storing hydrogen poses several problems. Therefore, in addition to hydrogen storage based on physical principles, there is increasing interest in storing hydrogen in a chemically bound form. Chemical hydrogen storage systems include solutions where hydrogen is stored and released based on chemical processes.

An example is the solution where hydrogen is chemically bound in metals in the form of metal hydrides (e.g. MgH_2, MgH_2–$LiAlH_4$, MgH_2–$LiBH_4$, $FeTiH_2$). The disadvantage of this

solution is that high temperatures are required to release the hydrogen due to the strong chemical bond between the metal and the hydrogen. If the process is repeated several times, it causes an unfavourable change in the structure of the storage metal.

Another example is a solution in which hydrogen atoms are covalently bonded to a central atom in a coordination hydrido complex and an additional metal ion stabilizes the complex. The best known of these are, for example, the compounds $LiBH_4$ and $LiAlH_4$. It can be stated that this solution basically provides higher hydrogen storage capacities than metal hydrides, however, reversibility raises problems with these compounds. Moreover, the release of hydrogen in many cases cannot be described as a single-step process.

Liquid organic hydrogen carriers (LOHC) are compounds that mostly contain hydrogen-poor, unsaturated or aromatic functional groups. Thus, these compounds can be saturated with hydrogen in the presence of a suitable catalyst, and the hydrogen can be then released from the resulting compound, also in the presence of a catalyst. Examples of liquid organic hydrogen carriers are toluene/methylcyclohexane, dibenzyl toluene/perhydrodibenzyl toluene, as well as the bicarbonate/formate system used in the present invention. These systems have a significant hydrogen storage capacity and hydrogen can be stored for long periods of time at ambient temperature and pressure with virtually no loss.

In a group of chemical hydrogen storage systems based on organic hydrogen carriers, different conditions (e.g. auxiliary materials or different catalysts) are needed for hydrogen storage and release, and two processes, which can be considered irreversible in themselves, form the complete system and together they enable hydrogen storage and release.

A special group of chemical hydrogen storage systems are systems in which the catalytic hydrogenation of a hydrogen-poor storage medium to a hydrogen-rich compound (charging step) and the dehydrogenation (discharging step) with reducing the hydrogen pressure and/or increasing the temperature are carried in the same device in a reversible reaction in the presence of the same catalyst. Such systems are referred to in the present application as chemical hydrogen accumulators, or hydrogen accumulators for short.

In the latter case, it is therefore a requirement that both hydrogenation (hydrogen storage) and dehydrogenation (hydrogen release) are efficiently catalyzed by the same catalyst, which can be either a heterogeneous or a homogeneous catalyst.

Furthermore, it is advantageous if the cyclic hydrogen charging and discharging of the hydrogen accumulator does not require the continuous or cyclic addition of any auxiliary materials (e.g. acids or bases). Overall, the operation of a chemical hydrogen accumulator is very similar to that of an electric accumulator.

As described above, a hydrogen accumulator must involve a reversible hydrogenation/dehydrogenation reaction in which the dynamic chemical equilibrium is not particularly favourable to either reactant. The bicarbonate/formate equilibrium in aqueous solution is well suited to this purpose:

$$HCO_3^-{}_{(aq)} + H_{2(aq)} \rightleftharpoons HCO_2^-{}_{(aq)} + H_2O_{(l)}.$$

Despite the relatively low hydrogen capacity of aqueous alkali formate salt solutions, the development of such hydrogen storage systems is highly advantageous compared to other methods of hydrogen storage due to the minimal safety risk.

During the operation of a hydrogen accumulator based on the bicarbonate-formate equilibrium, the reaction of bicarbonate may yield CO_2 according to the following equation:

$$2HCO_3^- = CO_3^{2-} + CO_2 + H_2O$$

The extent of this side reaction is strongly dependent on the concentration and cation of the bicarbonate salt, the catalyst used to store the hydrogen and the reaction temperature. However, in an unfavorable case, the CO_2 concentration may reach up to 30% by volume of the gas flow provided by the accumulator. This leads to a loss of storage material and may inhibit the use of stored hydrogen gas in fuel cells. Therefore, it can be seen that the CO_2 generated during accumulator discharge must be minimized (eliminated) by appropriately selecting the catalyst, formate salt and accumulator operating conditions.

The dehydrogenation of formate salts using Pd/C in aqueous systems was first described *by Wrighton et al.* (Stalder, C. J.; Chao, S.; Summers, D. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105* (*20*), 6318–6320. https://doi.org/10.1021/ja00358a026.), then it was studied by *Sasson et al.* (Wiener, H.; Sasson, Y.; Blum, J. *J. Mol. Catal.* **1986**, *35* (*3*), 277–284. https://doi.org/10.1016/0304-5102(86)87075-4.). The first detailed studies on using water-soluble Rh(I), Ru(II) and Ir(I) complexes as catalysts for the hydrogenation of bicarbonate in aqueous solution (without additives such as amines) were published in 1999 (Joó, F.;

Laurenczy, G.; Nádasdi, L.; Elek, J. *Chem. Commun.* **1999**, *No. 11*, 971–972. https://doi.org/10.1039/a902368b.). Furthermore, the homogeneous catalysis of hydrogenation of a bicarbonate suspension to formate in a phase transfer catalyzed toluene/water biphasic reaction system has been described (Rebreyend, C.; Pidko, E. A.; Filonenko, G. A. *Green Chem.* 2021, **23**, 8848–8852; https://doi.org/10.1039/D1GC02246F). The widespread use of aqueous solutions of HCO_2K as hydrogen storage material was proposed by *Sasson et al.* in 1986 (Zaidman, B.; Wiener, H.; Sasson, Y. *Int. J. Hydrog. Energy* **1986**, *11* (*5*), 341–347. https://doi.org/10.1016/0360-3199(86)90154-0.).

Plietker et al. described a hydrogen accumulator using [RuCl(PNNP)(acetonitrile)]PF_6 complex as a catalyst in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-1-ene) as a basic additive (Hsu, S.-F.; Rommel, S.; Eversfield, P.; Muller, K.; Klemm, E.; Thiel, W. R.; Plietker, B. *Angew. Chem. Int. Ed.* **2014**, *53* (*27*), 7074–7078. https://doi.org/10.1002/anie.201310972.). According to their solution, when the loading reaction, i.e. the hydrogenation of carbon dioxide/bicarbonate, is complete (indicated by no further pressure change), the reactor is cooled to room temperature and flushed with nitrogen. The resulting solution (DBU formate in toluene) can be stored for days at room temperature, and can be decomposed into a gas mixture of H_2 and CO_2 when heated to 100°C at ambient pressure, while the DBU is recovered. This hydrogen storage/release cycle is repeated five times without any significant change in the rate of the discharge process and the amount of H_2 delivered. According to the cited publication, the hydrogen accumulator described requires the addition of not only H_2 but also CO_2 to start each cycle. Furthermore, due to the large CO_2 excess, only about 15% of the CO_2 used is converted to DBU formate, and the rest is vented at the end of the hydrogenation step.

Recently, *Beller et al.* described a Mn(I)-pincer (clip, clamp) type complex capable of CO_2 hydrogenation and formate dehydrogenation in the presence of the potassium salt of lysine (LysK) in H_2O/THF solutions (Wei, D.; Sang, R.; Sponholz, P.; Junge, H.; Beller, M. *Nat. Energy* **2022**, *7* (*5*), 438–447. https://doi.org/10.1038/s41560-022-01019-4.). In the cited publication, it was described that in water/THF mixtures, several [$MnBr(CO)_2$(PNP)] complexes are active in both CO_2 hydrogenation and formic acid decomposition. In the presence of potassium salt of lysine (LysK), 2 000 000 catalytic cycle numbers (TONs) were observed during hydrogenation of CO_2 and 600 000 TONs during dehydrogenation of formic acid in a stability study of the catalyst over several cycles. The dehydrogenation was carried out

at 90°C and ambient pressure, and the hydrogenation was carried out at 85°C and an initial H_2 pressure of 80 bar. The operation of the accumulator was started by dehydrogenation of formic acid in the presence of an equivalent amount of LysK. At the end of this step, the gas phase was vented and analyzed, while the solution phase was subjected to hydrogenation. The LysK allowed the retention of more than 99.9% of the CO_2 produced during dehydrogenation of formic acid (internal carbon dioxide capture). The hydrogen storage and release steps can be repeated without the need to recharge CO_2 (or other components) between cycles. The operation of the described accumulator requires an amount of lysine equivalent to the concentration of formic acid to be obtained in the hydrogenation step. The accumulator was operated through 10 charge/discharge cycles, i.e. hydrogenation/dehydrogenation cycles on a 90.0 mmol scale without changing the reaction mixture.

Cao et al. have developed a fully aqueous hydrogen accumulator based on heterogeneous catalysis of HCO_2K/HCO_3K equilibrium under pressurized H_2 and pressure-free conditions (Bi, Q.-Y.; Lin, J.-D.; Liu, Y.-M.; Du, X.-L.; Wang, J.-Q.; He, H.-Y.; Cao, Y. *Angew. Chem. Int. Ed.* **2014**, *53* (*49*), 13583–13587. https://doi.org/10.1002/anie.201409500.). The catalyst comprised Pd nanoparticles on a reduced graphene oxide (rGO) support, which was found to be an active and durable catalyst for bicarbonate hydrogenation and formate dehydrogenation. HCO_2K was far superior to Na-, Li- or NH_4-formate with regard to its reactivity and stability. During hydrogenation of the HCO_3K content of 5 mL of aqueous 4.8 M HCO_3K solution containing 9.6 μmol Pd under $P(H_2)$ = 40 bar pressure, 7088 TONs was achieved (94.5% bicarbonate conversion). After decompression at 25 °C, the resulting formate solution was subjected to dehydrogenation by heating to 80 °C, thereby obtaining H_2 gas with nearly complete conversion of the formate in 40 min. This charge/discharge cycle was repeated six times without any impairment in accumulator performance. Furthermore, even at high HCO_2K concentrations (>8 M) and temperatures (>150 °C), only very small amount of CO_2 (<0.05 vol%) was produced. No formate decomposition occurred at 30°C or below, which allowed the rate of H_2 formation to be controlled by varying the temperature of the reaction mixture. According to the cited publication, 5 litres of a 4.8 M HCO_2K solution produces sufficient H_2 as fuel to a 1 kW fuel cell, provided that continuous regeneration or replenishment of the energy-rich formate solution can be ensured.

Recently, a hydrogen-dependent CO_2-reductase (HDCR) enzyme complex has been identified in *Acetobacterium woodii* that requires hydrogen to produce formic acid, while it

dehydrogenates HCO_2H into a mixture of H_2 and CO_2 in anaerobic atmosphere free of H_2 (Schuchmann, K.; Müller, V. *Science* **2013**, *342* (*6164*), 1382–1385. https://doi.org/10.1126/science.1244758.). *Müller* et al. designed a biocatalytic hydrogen accumulator using a resting *A. woodii* cell culture instead of the isolated HDCR enzyme (Schwarz, F. M.; Moon, J.; Oswald, F.; Müller, V. *Joule* **2022**, *6* (*6*), 1304–1319. https://doi.org/10.1016/j.joule.2022.04.020.). According to their solution, formic acid formation and H_2 release is carried out in the same bioreactor and the direction of the process is regulated by alternating the purge gas composition between a 45% H_2, 45% CO_2 and 10% N_2 (daytime) composition and a 100% N_2 (night-time) composition. During the "night-time" (16 h), the formic acid concentration decreased from 28 mM to 4.9 mM. The H_2 storage/discharge cycles were repeated for 15 days (360 h in total).

Patent document no. *US4067958* describes a process for producing hydrogen from fuel gas containing carbon monoxide and nitrogen or methane. The fuel gas is passed through an aqueous solution containing sodium or potassium carbonate and/or bicarbonate at a temperature of 400-600°F (204-315°C) and under a pressure of 20-150 atm to produce the corresponding formate. The formate solution is then catalytically decomposed to form hydrogen and carbonate and/or bicarbonate. The cited patent document also describes the apparatus implementing the process. The used catalysts may be transition metals, their oxides or sulphides on an alkali-resistant support.

In patent document no. *US20120321550* mononuclear transition metal complexes that can be used in hydrogen storage processes are disclosed in great detail. In the cited document, it is described that hydrogen is evolved from alcohols and then the starting alcohol is recovered from the resulting aldehyde by hydrogenation with a similar catalyst. Furthermore, the $HCO_2H/HCO_2^-/CO_2/HCO_3^-$ equilibrium has been successfully applied in these systems. Due to the pH-sensitivity of the ligand, the key issue in this system is to keep the pH constant. Although, in the systems described in the cited patent document, the formate/hydrogen carbonate cycle plays a role, the catalyst family used has a different structure than the catalysts described in the present invention. In the catalyst according to the cited document, one of the ligands comprises two isolated aromatic rings, each of which is linked to the central metal by one carbon atom or by one carbon atom and one nitrogen atom.

Romero et al. [Romero, E.A. et al. Nature Catalysis 1(10), 743-747 (2018)] describe Cu complexes that catalyze the hydrogenation of CO_2 in tetrahydrofuran (THF) solvent in the presence of a Lewis acid-base pair [typically $B(C_6F_5)_3$ and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU)]. Specific examples include Cu complexes, where one of the ligands is BH_4^- and the other ligand is an NHC or a cyclic (alkyl)(amino)carbene. However, the system used for hydrogenation according to the cited document is different from the system based on formate-bicarbonate equilibrium according to the present invention.

Patent document no. *US 9556211 B2* describes a catalyst that catalyses the dehydrogenation of formic acid and the hydrogenation of CO_2 in an aqueous medium. The catalyst is a metal complex, where the central atom is Ir, Fe, Rh or Ru, and where the ligands include carbonyl, hydride and tertiary phosphine. In the embodiments of the cited document, only Ir complexes are included.

In their publication [Gonsalvi, L. et al. Homogeneously Catalyzed CO_2 Hydrogenation to Formic Acid/Formate with Non-precious Metal Catalysts (2021)], Gonsalvi et al. summarize which non-precious metal catalysts have been successfully used to hydrogenate CO_2 or bicarbonate to formic acid or formate up to the time of the cited publication. Various complexes of Fe, Co, Ni, Cu, Mn, Re, Mo and W are described in the cited document, but these are different from the complexes used in the present invention.

Patent document no. *DE102006030449* discloses an apparatus usable for reversible hydrogen storage. The apparatus is based on the capture and release of hydrogen. The hydrogen is captured by reducing potassium carbonate and/or potassium bicarbonate in aqueous solution to potassium formate by electric current in the presence of hydrogen gas and a ZnO or ZnO\TiO_2 catalyst. The hydrogen release is carried out from an aqueous solution of potassium formate, formic acid or mixtures of these using platinum or palladium catalysts.

Patent document no. *WO2012143372* discloses a process for selective decomposition of formic acid to produce hydrogen using a transition metal complex catalyst coordinating at least one tripodal tetradentate ligand. According to the cited document, the complexing metals are iridium, palladium, platinum, ruthenium, rhodium, cobalt and iron. The process can be carried out at low/medium temperature (below 100°C) and normal pressure (1 bar) and yields a gas mixture of H_2:CO_2 in a volume ratio of 1:1. The carbon monoxide content of the resulting gas mixture is below the threshold that is still accepted for use in so-called H_2/O_2

PEM (Proton-Exchange Membrane) fuel cells. The structure of the catalysts described in the cited document differs from the structure of the catalysts described in the specification.

Patent document no. *US10944119B2* discloses a process that allows the storage and release of hydrogen. Although, the document mentions the bicarbonate-formate cycle for hydrogen storage and release, but in the hydrogen release process, the transition metal catalyst (ruthenium-containing complex) used is dissolved in an organic solvent or solvent mixture and the resulting bicarbonate is formed in the aqueous phase separated from the organic solution containing the catalyst. As to the hydrogenation of the bicarbonate, it is disclosed only that this step can also be facilitated by the same catalyst system as the decomposition of the formate.

European patent document no. *EP3065865B1* describes a process for the production and storage of hydrogen. Hydrogen is produced by the catalytic decomposition of potassium formate from a concentrated aqueous solution, thereby obtaining bicarbonate slurry and hydrogen. The mixture of bicarbonate slurry and catalyst is then oxidized with oxygen or air to regenerate the catalyst. Hydrogen storage is carried out by reducing the oxidant-treated potassium bicarbonate slurry including the regenerated catalyst in the presence of hydrogen. The catalyst is palladium deposited on a carbon support, therefore this solution is different from the solution according to the invention.

International patent document no. *WO2008032985A1* discloses an organometallic compound for the storage of hydrogen. Said compound is a metal hydride complex of general formula A-$(OMH_m)_n$, where the transition metal (M) is attached to the oxygen atom of the organic molecule (A) containing a hydroxyl group. The transition metal is at least bivalent, the value of m is one less than the valence of the metal atom, and the value of n can be an integer from 1 to 1000. Examples of organic compounds containing a hydroxyl group include ethylene glycol, trimethylene glycol, glycerol, and hydroxyl-containing aryl derivatives such as phloroglucinol. The solution according to the cited document differs from the solution according to the invention as it is not based on formate-bicarbonate equilibrium.

International patent document no. *WO2015040440* describes iridium-containing catalysts of general formula [IrCl(cod)(NHC)] + nP (n = 2, 3 or 4) or [Ir(cod)(NHC)(P)] + nP (n = 1, 2 or 3), where cod is 1,5-cyclooctadiene; NHC is N-heterocyclic carbene and P is 1,3,5-triaza-7-phosphaadamantane (pta), monosulfonated triphenylphosphine (*m*tppms),

trisulfonated triphenylphosphine (*m*tppts), or tetrasulfonated diphenylphosphinopropane (dpppts). The described catalysts are suitable for the decomposition of formates in an aqueous reaction mixture and the production of hydrogen gas free of CO_x by-products or for the hydrogenation of bicarbonates.

International patent document no. *WO2023275578* discloses a process for hydrogenation of bicarbonate in aqueous media and for decomposition of formate in aqueous media to release hydrogen. Hydrogenation of bicarbonate is carried out in such a way that CO_2 present in the gas space. The catalysts used for hydrogenation and hydrogen release are also iridium-containing catalysts of general formula $[Ir(cod)(NHC)P_a] + nP_b$, where cod is 1,5-cyclooctadiene, NHC is N-heterocyclic carbene and P_a and P_b are 1,3,5-triaza-7-phosphaadamantane (pta), monosulfonated triphenylphosphine (*m*tppms) or trisulfonated triphenylphosphine (*m*tppts).

Although, the hydrogenation/dehydrogenation can be effectively performed in the bicarbonate/formate system with the previously described iridium-containing catalysts on a laboratory scale, it should be noted that iridium is rare in the earth's crust and is therefore only available at a high cost and in limited quantities, which poses a serious obstacle to its widespread use on an industrial scale.

THE TECHNICAL PROBLEM TO BE SOLVED BY THE INVENTION

The technical problem to be solved by the invention is to provide economically advantageous, cost-effective catalysts that can be conveniently produced on an industrial scale, and a process for a hydrogen gas storage system and a hydrogen gas release system,

a) where hydrogen gas storage is carried out by hydrogenation of hydrogencarbonates in the presence of a catalyst in an aqueous medium and hydrogen gas release without CO_x by-products is carried out by decomposition of formates in the presence of a catalyst in an aqueous medium;

b) and where the hydrogen gas storage and hydrogen gas release are carried out using the same catalyst, preferably the hydrogen gas storage and the hydrogen gas release are carried out in a single system.

THE INSIGHT ON WHICH THE INVENTION IS BASED

The aforementioned objectives are achieved by a solution based on the surprising insight that for the hydrogenation of hydrogencarbonates, which step provides the storage of hydrogen gas, and for the decomposition of formates, which step provides the release of hydrogen gas, the catalyst described in the invention is used under the reaction conditions of the invention, both steps being carried out without the continuous or cyclic addition of auxiliary substances (e.g. acids or bases). Surprisingly, we have found that catalysts comprising a complex containing a metal central atom, which is a non-platinum transition metal, p-field metal or f-field metal, and at least one strong sigma-donor ligand selected from N-heterocyclic carbene ligands and water-soluble phosphine ligands, are suitable for catalyzing said reactions.

To substantiate the surprising effect achieved by our invention, we emphasize that, in a complex compound used as a catalyst, is not an obvious solution to replace the metal atom constituting the central metal, in particular a platinum group metal atom, which is known to be efficient in the field of catalysts, by another metal atom, in particular a non-platinum group metal atom, since the usefulness of the complex obtained by such modification as a catalyst in a given reaction system cannot be predicted.

BRIEF DESCRIPTION OF THE INVENTION

The scope of protection of the invention is defined in the appended claims.

DEFINITIONS

In the context of the invention, non-platinum group transition metals are those transition metals that do not belong to the platinum group. Examples of non-platinum group transition metals include titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, molybdenum and yttrium.

In the context of the invention, "carbene" means a molecule comprising a bivalent neutral carbon atom. Typical carbene compounds are (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), 1-R^1-3-R^2-imidazol-2-ylidene, 1-R^1-3-R^2-imidazolin-2-ylidene and 1-R^1-3-R^2-benzimidazol-2-ylidene, wherein R^1 and R^2 are each independently a straight or branched chain alkyl group of 1 to 6 carbon atoms, or a benzyl group, or a phenyl group, which is unsubstituted or substituted with an alkyl group of 1 to 6 carbon atoms.

Examples of carbenes include N-heterocyclic carbenes (NHCs) such as 1-ethyl-3-methylimidazol-2-ylidene (emim); 1-butyl-3-methylimidazol-2-ylidene (bmim); 1-hexyl-3-methylimidazol-2-ylidene (hexmim) and 1-benzyl-3-methylimidazol-2-ylidene (Bnmim); (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron). We note that N-heterocyclic carbenes, like phosphine ligands, belong to strong sigma donors.

In the context of the invention, the term "**NHC** precursor" refers to precursors of **NHC** ligands as defined above, which are suitable for incorporation of said **NHC** ligands into complexes. Typical **NHC** precursors are salts consisting of the protonated form of **NHC** ligands and an anion, wherein the anion is, for example, halide, acetate, dicyanamide, tetrafluoroborate, hexafluorophosphate, methanesulfonate. We note that although the salts mentioned are actually the salts consisting of the protonated form of **NHC** compounds as defined above and an anion, in the names found in the literature, often only the anion is indicated. For example, **NHC** hydrochlorides are often referred to in the literature as **NHC** chlorides, though they refer to the same compound.

Examples of **NHC** precursors are (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), and salts of 1-R^1-3-R^2-imidazolium, 1-R^1-3-R^2-imidazolinium and 1-R^1-3-R^2-benzimidazolium, wherein R^1 and R^2 are each independently a straight or branched chain alkyl group of 1 to 6 carbon atoms or a benzyl group, or a phenyl group, which is unsubstituted or substituted with an alkyl group of 1 to 6 carbon atoms.

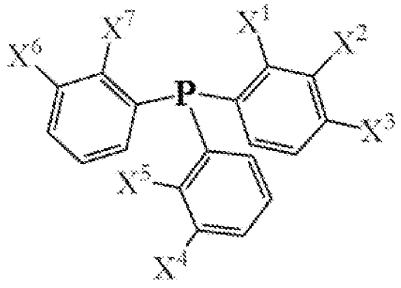
Specific examples of **NHC** precursors include 1-ethyl-3-methylimidazolium chloride (emimCl); 1-ethyl-3-methylimidazolium acetate; 1-butyl-3-methylimidazolium chloride (bmimCl); 1-hexyl-3-methylimidazolium chloride (hexmimCl) and 1-benzyl-3-methylimidazolium chloride (BnmimCl); and (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron).

Water-soluble phosphine ligands are well known to the person skilled in the art.

A group of these are tertiary phosphines whose solubility in water is ensured by polar or ionic groups, i.e. they contain e.g. a hydroxyalkyl group, an alkyl group substituted with a sulphonato group, or a phenyl group substituted with a sulphonato group. It is well known to the person skilled in the art that in order to achieve water solubility, the presence of a single

sulphonato group-bearing moiety in the molecule is sufficient, whereas several hydroxyl groups are usually required (e.g. several hydroxyalkyl groups).

More specifically, a group of tertiary phosphines are sulphonated triphenylphosphines, which, due to the presence of negatively charged sulphonate groups, also contain counterions (typically Li, Na, K or Cs ions) and are therefore chemically considered to be salts. In the context of the invention, be the terms Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *ortho* position (*o*tppms, *o*tppds, *o*tppts), Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts), and Li, Na, K or Cs salt of a triphenylphosphine, which is monosulfonated in the *para* position (*p*tppms), compounds according to formula (1) below are meant:



formula (1)

wherein the meaning of X^1-X^7 in the formula is summarised in Table 1 below:

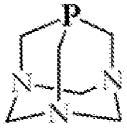
Table 1

	X^1	X^2	X^3	X^4	X^5	X^6	X^7
*o*tppms	SO_3Y	H	H	H	H	H	H
*o*tppds	SO_3Y	H	H	H	SO_3Y	H	H
*o*tppts	SO_3Y	H	H	H	SO_3Y	H	SO_3Y
*m*tppms	H	SO_3Y	H	H	H	H	H
*m*tppds	H	SO_3Y	H	SO_3Y	H	H	H
*m*tppts	H	SO_3Y	H	SO_3Y	H	SO_3Y	H
*p*tppms	H	H	SO_3Y	H	H	H	H

Y = Li, Na, K or Cs.

In the context of the invention, water-soluble phosphine ligands include O, N or S heterocyclic compounds as well, which, in addition to said atoms, also contain a trivalent phosphorus, P(III) atom in the ring (hereafter referred to as cyclic tertiary phosphines). Their water solubility is ensured by the strong hydrogen bonding interaction between the non-P (i.e. O, N and S) heteroatoms and water.

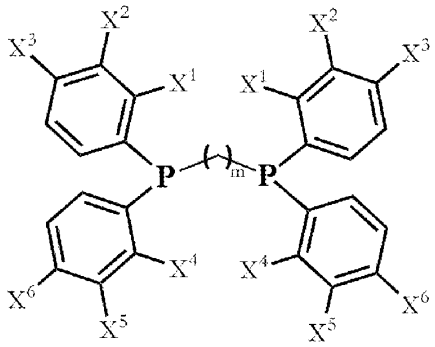
In the context of the invention, non-limiting examples of "cyclic tertiary phosphines" include phosphaazaadamantane compounds, one example of which is 1,3,5-triaza-7-phosphaadamantane (pta) according to formula (2) below:



formula (2).

A further group of water-soluble phosphine ligands are phosphines of the general formula R^4_2P-*bridge*-PR^5_2, whose water solubility is subject to considerations similar to those described for tertiary phosphines, with the proviso that at least one of the R^4_2P and PR^5_2 groups carries a group or groups of a polar or ionic nature which confer water solubility to the ligand.

In the context of the invention, non-limiting examples of R^4_2P-*bridge*-PR^5_2 phosphines include the compounds of formula (3) below:



formula (3)

wherein the meaning of X^1-X^7 in formula (3) is summarised in Table 2 below, and where m in formula (3) is an integer of 1 to 6, i.e. in the formula R^4_2P-*bridge*-PR^5_2 the "*bridge*" is an alkylene group of 1 to 6 carbon atoms.

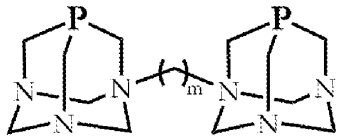
Table 2

X^1	X^2	X^3	X^4	X^5	X^6
SO_3Y	H	H	H	H	H
SO_3Y	H	H	SO_3Y	H	H
H	SO_3Y	H	H	H	H
H	SO_3Y	H	H	SO_3Y	H
H	H	SO_3Y	H	H	H
H	H	SO_3Y	H	H	SO_3Y

Y = Li, Na, K or Cs

Water-soluble phosphine ligands also include ring compounds linked with bridging structures, such as bridged diphosphine derivatives of cyclic tertiary phosphines, the so-called covalently bonded bridged cyclic tertiary phosphines.

Non-limiting examples of "covalently bonded bridged cyclic tertiary phosphines" in the context of the invention include compounds according to formula (4) below:



formula (4)

where m in formula (4) is an integer from 1 to 6.

In the context of the invention, "cycloalkadiene" is understood to be a cyclic hydrocarbon containing two double bonds.

In the context of the invention, "π-donor aromatic hydrocarbon ligand" is understood to be a compound containing a single benzene ring, wherein the benzene ring is optionally substituted with an alkyl group. Examples of π-donor aromatic hydrocarbon ligands include benzene and 4-isopropyltoluene.

DETAILED DESCRIPTION OF THE INVENTION

The object of our invention is the use of an isolated or non-isolated (*in situ* generated) catalyst comprising an **M** central metal and at least one strong sigma-donor ligand selected from the group consisting of **NHC** N-heterocyclic carbene ligands and **Pws** water-soluble phosphine ligands, in a process for storing hydrogen gas and/or in a process for releasing hydrogen gas, wherein the storage of hydrogen gas and the release of hydrogen gas are based on formate-bicarbonate equilibrium, wherein:

M is selected from non-platinum transition metals, p-field metals and f-field metals;

NHC is an N-heterocyclic carbene ligand, preferably selected from the group consisting of: 1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), 1-R^1-3-R^2-imidazol-2-ylidene, 1-R^1-3-R^2-imidazolin-2-ylidene and 1-R^1-3-R^2-benzimidazol-2-ylidene, wherein R^1 and R^2 are each independently a straight or branched chain alkyl group of 1 to 6 carbon atoms or a benzyl group, or a phenyl group, which is unsubstituted or substituted with an alkyl group of 1 to 6 carbon atoms;

Pws is a water soluble phosphine ligand selected from the group consisting of:

a tertiary phosphine of general formula $PR^1R^2R^3$, wherein R^1, R^2 and R^3 are independently a straight or branched chain alkyl group of 1 to 5 carbon atoms or a phenyl group, wherein the alkyl group may be substituted with an OH group or a sulphonato group and the phenyl group may be substituted with an alkyl group of 1 to 6 carbon atoms and/or a sulphonato group, provided that at least one of R^1, R^2 and R^3 carries an OH group or a sulphonato group; or

a cyclic tertiary phosphine; or

a diphosphine of general formula $R^4{}_2P$-*bridge*-$PR^5{}_2$ wherein R^4 and R^5 are independently a straight or branched chain alkyl group of 1 to 5 carbon atoms, or a phenyl group, wherein the alkyl group may be substituted with an OH group or a sulfonato group, and the phenyl group

may be substituted with an alkyl group of 1 to 6 carbon atoms or a sulfonato group, wherein PR^4_2 and PR^5_2 may have the same or different meanings, provided that at least one of R^4 and R^5 carries an OH group or a sulphonato group; wherein the *bridge* group is a straight chain alkylene group of 1 to 6 carbon atoms, preferably a methylene, ethylene, propylene, butylene or hexylene group; or

a diphosphine, which comprises cyclic tertiary phosphino groups linked by a covalent bonded bridge.

Throughout this description, unless otherwise indicated, the term "catalyst" is used to include both non-isolated (*in situ* generated) catalysts and isolated catalysts.

In one embodiment of the invention, **M** in the catalyst is selected from the group consisting of non-platinum transition metals, lanthanum and tin.

In a further embodiment of the invention, **M** in the catalyst is selected from the group consisting of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, yttrium, molybdenum, lanthanum and tin.

In a further embodiment of the invention, **M** in the catalyst is selected from the group consisting of non-platinum transition metals.

In a further embodiment of the invention, **M** in the catalyst is selected from titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, yttrium and molybdenum.

In a further embodiment of the invention, **M** in the catalyst is lanthanum.

In a further embodiment of the invention, **M** in the catalyst is tin.

In a further embodiment of the invention, **M** in the catalyst is selected from titanium, vanadium, chromium, manganese, iron, cobalt, nickel and copper.

In a further embodiment of the invention, **M** in the catalyst is selected from manganese, iron, cobalt, nickel and copper.

In one embodiment of the invention, **NHC** in the catalyst is selected from the group consisting of: (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), 1,3-dimethylimidazol-2-ylidene, 1-ethyl-3-methylimidazol-2-ylidene (emim), 1-methyl-3-

propylimidazol-2-ylidene, 1-butyl-3-methylimidazol-2-ylidene (bmim), 1-methyl-3-pentylimidazol-2-ylidene, 1,3-diethylimidazol-2-ylidene, 1-ethyl-3-propylimidazol-2-ylidene, 1-ethyl-3-butylimidazol-2-ylidene, 1-ethyl-3-pentylimidazol-2-ylidene, 1,3-dipropylimidazol-2-ylidene, 1-propyl-3-butylimidazol-2-ylidene, 1-propyl-3-pentylimidazol-2-ylidene, 1,3-dibutylimidazol-2-ylidene, 1-butyl-3-pentylimidazol-2-ylidene, 1,3-dipentylimidazol-2-ylidene; 1,3-diizopropylimidazol-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)imidazol-2-ylidene; 1-methyl-3-phenylimidazol-2-ylidene, 1-ethyl-3-phenylimidazol-2-ylidene, 1-propyl-3-phenylimidazol-2-ylidene, 1-butyl-3-phenylimidazol-2-ylidene, 1-pentyl-3-phenylimidazol-2-ylidene, 1,3-diphenylimidazol-2-ylidene; 1-benzyl-3-methylimidazol-2-ylidene (Bnmim), 1-hexyl-3-methylimidazol-2-ylidene (hexmim), 1,3-dimethylimidazolin-2-ylidene, 1-methyl-3-ethylimidazolin-2-ylidene, 1-methyl-3-propylimidazolin-2-ylidene, 1-methyl-3-butylimidazolin-2-ylidene, 1-methyl-3-pentylimidazolin-2-ylidene, 1,3-diethylimidazolin-2-ylidene, 1-ethyl-3-propylimidazolin-2-ylidene, 1-ethyl-3-butylimidazolin-2-ylidene, 1-ethyl-3-pentylimidazolin-2-ylidene, 1,3-dipropylimidazolin-2-ylidene, 1-propyl-3-butylimidazolin-2-ylidene, 1-propyl-3-pentylimidazolin-2-ylidene, 1,3-dibutylimidazolin-2-ylidene, 1-butyl-3-pentylimidazolin-2-ylidene, 1,3-dipentylimidazolin-2-ylidene; 1,3-diizopropylimidazolin-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)imidazolin-2-ylidene; 1-methyl-3-phenylimidazolin-2-ylidene, 1-ethyl-3-phenylimidazolin-2-ylidene, 1-propyl-3-phenylimidazolin-2-ylidene, 1-butyl-3-phenylimidazolin-2-ylidene, 1-pentyl-3-phenylimidazolin-2-ylidene, 1,3-diphenylimidazolin-2-ylidene; 1,3-dimethylbenzimidazol-2-ylidene, 1-methyl-3-ethylbenzimidazol-2-ylidene, 1-methyl-3-propylbenzimidazol-2-ylidene, 1-methyl-3-butylbenzimidazol-2-ylidene, 1-methyl-3-pentylbenzimidazol-2-ylidene, 1,3-diethylbenzimidazol-2-ylidene, 1-ethyl-3-propylbenzimidazol-2-ylidene, 1-ethyl-3-butylbenzimidazol-2-ylidene, 1-ethyl-3-pentylbenzimidazol-2-ylidene, 1,3-dipropylbenzimidazol-2-ylidene, 1-propyl-3-butylbenzimidazol-2-ylidene, 1-propyl-3-pentylbenzimidazol-2-ylidene, 1,3-dibutylbenzimidazol-2-ylidene, 1-butyl-3-pentylbenzimidazol-2-ylidene, 1,3-dipentylbenzimidazol-2-ylidene; 1,3-diizopropylbenzimidazol-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)benzimidazol-2-ylidene; 1-methyl-3-phenylbenzimidazol-2-ylidene, 1-ethyl-3-phenylbenzimidazol-2-ylidene, 1-propyl-3-phenylbenzimidazol-2-ylidene, 1-butyl-3-phenylbenzimidazol-2-ylidene, 1-pentyl-3-phenylbenzimidazol-2-ylidene and 1,3-diphenylbenzimidazol-2-ylidene. For the preparation of non-isolated catalysts, appropriate precursors of the listed NHC ligands can be used as NHC precursors.

In a further embodiment of the invention, **NHC** in the catalyst is selected from the group consisting of: 1-ethyl-3-methylimidazol-2-ylidene (emim); 1-butyl-3-methylimidazol-2-ylidene (bmim); 1-hexyl-3-methylimidazol-2-ylidene (hexmim) and 1-benzyl-3-methylimidazol-2-ylidene (Bnmim); and (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron).

In one embodiment of the invention, **Pws** in the catalyst is selected from the group consisting of:

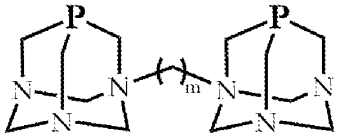
a tertiary phosphine of general formula $PR^1R^2R^3$ selected from the group consisting of: $P(CH_2OH)_3$ [tris(hydroxymethyl)phosphine], Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *ortho* position (*o*tppms, *o*tppds, *o*tppts); Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts); and Li, Na, K or Cs salt of a triphenylphosphine, which is monosulfonated in the *para* position (*p*tppms); and

1,3,5-triaza-7-phosphaadamantane (pta).

In another embodiment of the invention, **Pws** in the catalyst is selected from the group consisting of:

a phosphine of general formula R^4_2P-*bridge*-PR^5_2, wherein PR^4_2 and PR^5_2 are independently selected from: $P(CH_2OH)_2$ (bis(hydroxymethyl)phosphino group), PPh_2 (diphenylphosphino group), Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *ortho* position; Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *meta* position; Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *para* position, *'bridge'* represents an alkylene group of 1 to 6 carbon atoms; and

compounds according to formula (4):



formula (4)

where m in formula (4) is an integer from 1 to 6.

In a further embodiment of the invention, **Pws** in the catalyst is selected from the group consisting of Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts); 1,3,5-triaza-7-phosphaadamantane (pta).

In a further embodiment of the invention, **Pws** in the catalyst is selected from the group consisting of tetrasulfonated 1,2-bis(diphenylphosphino)ethane (dppets), tetrasulfonated 1,3-bis(diphenylphosphino)propane (dpppts), and the compound of formula (4).

According to an embodiment, the isolated or non-isolated (*in situ* generated) catalyst according to the invention corresponds to general formula (I) (II) or (III):

$$\mathbf{[M(NHC)_n(Pws)_p(L^1)_q(L^2)_r]}\ \text{(I), or}$$

$$\mathbf{[Fe_3(NHC)_{n'}(Pws)_{p'}(L^1)_{q'}(L^2)_{r'}]}\ \text{(II), or}$$

$$\mathbf{[Co_2(NHC)_{n''}(Pws)_{p''}(L^1)_{q''}(L^2)_{r''}]}\ \text{(III),}$$

wherein

M, NHC and **Pws** are as defined above;

$\mathbf{L^1}$ is a negatively charged ligand, preferably selected from the group consisting of: H^-, F^-, Cl^-, Br^-, I^-, OH^-, BF_4^-, PF_6^-, HCO_3^- (hydrogencarbonate), HCO_2^- (formate), $CH_3CO_2^-$ (acetate), $[CH_3COCHCOCH_3]^-$ (acetylacetonate), cyanide, isocyanide, nitrite, nitrate, thiocyanate, and isothiocyanate; SO_4^{2-} and O^{2-};

$\mathbf{L^2}$ is a neutral (non-ionic) ligand selected from the group consisting of: H_2O, CO (carbonyl); MeOH; dimethylsulfoxide or acetonitrile; a cycloalkadiene of 5 to 10 ring members, optionally substituted with one or more substituents selected from alkyl groups of 1 to 5 carbon atoms and phenyl groups; a π-donor aromatic hydrocarbon ligand of 6 to 10 carbon atoms; and

in general formula (I), n, p, q and r are 0, 1, 2, 3 or 4, provided that n + p is at least 1 and $n + p + q + r \leq 8$;

in general formula (II), n' is 0 or 1, p' is 1, 2 or 3, q' is 0, r' = 12-n'-q'-r'-p';

in general formula (III), n" is 0 or 1, p" is 1 or 2, q" is 0, r" = 8-n"-q"-r"-p";

wherein, if n, p, q, r, n', p', q', r', n", p", q" and/or r" are greater than 1, then **NHC**, **Pws**, $\mathbf{L^1}$ and/or $\mathbf{L^2}$ may be the same or different.

In the general formula (I), $\mathbf{L^1}$ represents a negatively charged ligand. Suitable negatively charged ligands are well known to the person skilled in the art. In an embodiment of the invention, $\mathbf{L^1}$ is selected from the group consisting of: H^-, F^-, Cl^-, Br^-, I^-, OH^-, BF_4^-, PF_6^-, HCO_3^- (hydrogencarbonate), HCO_2^- (formate), $CH_3CO_2^-$ (acetate), $[CH_3COCHCOCH_3]^-$ (acetylacetonate), cyanide, isocyanide, nitrite, nitrate, thiocyanate, and isothiocyanate; SO_4^{2-} and O^{2-}.

In a further embodiment of the invention, in general formula (I), $\mathbf{L^1}$ is H^-, F^-, Cl^-, Br^-, I^-, BF_4^-, PF_6^-, $CH_3CO_2^-$ (acetate), SO_4^{2-} or O^{2-}.

In a further embodiment of the invention, in general formula (I), $\mathbf{L^1}$ is H^-, F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$ (acetate), SO_4^{2-} or O^{2-}.

In a further embodiment of the invention, in general formula (I), $\mathbf{L^1}$ is F^-, Cl^-, Br^-, I^-, SO_4^{2-} or O^{2-}.

In another embodiment of the invention, in general formula (I), $\mathbf{L^1}$ is H^-, F^-, Cl^-, Br^-, I^- or $CH_3CO_2^-$ (acetate).

In the general formula (I), (II) or (III), $\mathbf{L^2}$ represents a neutral ligand. Suitable ligands are well known to the person skilled in the art. In one embodiment of the invention, $\mathbf{L^2}$ is selected from the group consisting of: H_2O, CO (carbonyl); MeOH; dimethylsulfoxide or acetonitrile; a cycloalkadiene of 5 to 10 ring members, optionally substituted with one or more substituents selected from alkyl groups of 1 to 5 carbon atoms and phenyl groups; a π-donor aromatic hydrocarbon ligand of 6 to 10 carbon atoms.

In a further embodiment of the invention, the optionally substituted cycloalkadiene of 5 to 10 ring members is selected from the group consisting of: 1,5-cycloalkadiene, cyclopentadiene, 1,2,3,4,5-pentamethylcyclopentadiene and 1,2,3,4,5-pentaphenylcyclopentadiene.

In a further embodiment of the invention, said π-donor aromatic hydrocarbon ligand of 6 to 10 carbon atoms is selected from benzene and 4-isopropyltoluene.

In a further embodiment of the invention, in general formula (I), (II) or (III), $\mathbf{L^2}$ is CO, H_2O, MeOH, CH_3CN or dimethyl sulfoxide.

In a further embodiment of the invention, $\mathbf{L^2}$ is CO, H_2O, MeOH or CH_3CN.

In a further embodiment of the invention, $\mathbf{L^2}$ is CO or H_2O.

In a further embodiment of the invention, in general formula (I), n and p are 0, 1 or 2; q is 0, 1, 2, 3 or 4; and r is 0, 1, 2, 3 or 4, provided that n + p is at least 1. Preferably n + p + q + r $\leq$8.

In another embodiment, n+p in the general formula (I) is 1, 2 or 3. In a further embodiment, n+p+q+r $\leq$6.

In a further embodiment of the invention, in general formula (I), (II) or (III)

NHC is selected from the group consisting of: (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), 1,3-dimethylimidazol-2-ylidene, 1-ethyl-3-methylimidazol-2-ylidene (emim), 1-methyl-3-propylimidazol-2-ylidene, 1-butyl-3-methylimidazol-2-ylidene (bmim), 1-methyl-3-pentylimidazol-2-ylidene, 1,3-diethylimidazol-2-ylidene, 1-ethyl-3-propylimidazol-2-ylidene, 1-ethyl-3-butylimidazol-2-ylidene, 1-ethyl-3-pentylimidazol-2-ylidene, 1,3-dipropylimidazol-2-ylidene, 1-propyl-3-butylimidazol-2-ylidene, 1-propyl-3-pentylimidazol-2-ylidene, 1,3-dibutylimidazol-2-ylidene, 1-butyl-3-pentylimidazol-2-ylidene, 1,3-dipentylimidazol-2-ylidene; 1,3-diizopropylimidazol-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)imidazol-2-ylidene; 1-methyl-3-phenylimidazol-2-ylidene, 1-ethyl-3-phenylimidazol-2-ylidene, 1-propyl-3-phenylimidazol-2-ylidene, 1-butyl-3-phenylimidazol-2-ylidene, 1-pentyl-3-phenylimidazol-2-ylidene, 1,3-diphenylimidazol-2-ylidene; 1-benzyl-3-methylimidazol-2-ylidene (Bnmim), 1-hexyl-3-methylimidazol-2-ylidene (hexmim), 1,3-dimethylimidazolin-2-ylidene, 1-methyl-3-ethylimidazolin-2-ylidene, 1-methyl-3-propylimidazolin-2-ylidene, 1-methyl-3-butylimidazolin-2-ylidene, 1-methyl-3-pentylimidazolin-2-ylidene, 1,3-diethylimidazolin-2-ylidene, 1-ethyl-3-propylimidazolin-2-ylidene, 1-ethyl-3-butylimidazolin-2-ylidene, 1-ethyl-3-pentylimidazolin-2-ylidene, 1,3-dipropylimidazolin-2-ylidene, 1-propyl-3-butylimidazolin-2-ylidene, 1-propyl-3-pentylimidazolin-2-ylidene, 1,3-dibutylimidazolin-2-ylidene, 1-butyl-3-pentylimidazolin-2-ylidene, 1,3-dipentylimidazolin-2-ylidene; 1,3-diizopropylimidazolin-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)imidazolin-2-ylidene; 1-methyl-3-phenylimidazolin-2-ylidene, 1-ethyl-3-

phenylimidazolin-2-ylidene, 1-propyl-3-phenylimidazolin-2-ylidene, 1-butyl-3-phenylimidazolin-2-ylidene, 1-pentyl-3-phenylimidazolin-2-ylidene, 1,3-diphenylimidazolin-2-ylidene; 1,3-dimethylbenzimidazol-2-ylidene, 1-methyl-3-ethylbenzimidazol-2-ylidene, 1-methyl-3-propylbenzimidazol-2-ylidene, 1-methyl-3-butylbenzimidazol-2-ylidene, 1-methyl-3-pentylbenzimidazol-2-ylidene, 1,3-diethylbenzimidazol-2-ylidene, 1-ethyl-3-propylbenzimidazol-2-ylidene, 1-ethyl-3-butylbenzimidazol-2-ylidene, 1-ethyl-3-pentylbenzimidazol-2-ylidene, 1,3-dipropylbenzimidazol-2-ylidene, 1-propyl-3-butylbenzimidazol-2-ylidene, 1-propyl-3-pentylbenzimidazol-2-ylidene, 1,3-dibutylbenzimidazol-2-ylidene, 1-butyl-3-pentylbenzimidazol-2-ylidene, 1,3-dipentylbenzimidazol-2-ylidene; 1,3-diizopropylbenzimidazol-2-ylidene; 1,3-di(2,4,6-trimethylpheny)lbenzimidazol-2-ylidene; 1-methyl-3-phenylbenzimidazol-2-ylidene, 1-ethyl-3-phenylbenzimidazol-2-ylidene, 1-propyl-3-phenylbenzimidazol-2-ylidene, 1-butyl-3-phenylbenzimidazol-2-ylidene, 1-pentyl-3-phenylbenzimidazol-2-ylidene and 1,3-diphenylbenzimidazol-2-ylidene;

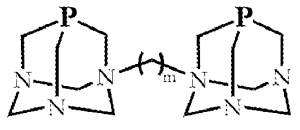
Pws is selected from the group consisting of:

a tertiary phosphine of general formula $PR^1R^2R^3$ selected from the group consisting of: $P(CH_2OH)_3$ [tris(hydroxymethyl)phosphine], Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *ortho* position (*o*tppms, *o*tppds, *o*tppts); Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts); and Li, Na, K or Cs salt of a triphenylphosphine, which is monosulfonated in the *para* position (*p*tppms); and

1,3,5-triaza-7-phosphadamantane (pta);

a phosphine of general formula R^4_2P-*bridge*-PR^5_2, wherein PR^4_2 and PR^5_2 are independently selected from: $P(CH_2OH)_2$ (bis(hydroxymethyl)phosphino group), PPh_2 (diphenylphosphino group), Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *ortho* position; Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *meta* position; Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *para* position; and

a compound of formula (4):

 (4),

where m is an integer from 1 to 6;

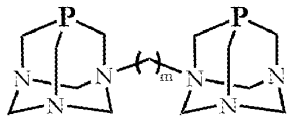
L[1] is selected from the group consisting of: H^-, F^- Cl^-, Br^-, I^-, OH^-, BF_4^-, PF_6^-, HCO_3^- (hydrogencarbonate), HCO_2^- (formate), $CH_3CO_2^-$ (acetate), $[CH_3COCHCOCH_3]^-$ (acetylacetonate), cyanide, isocyanide, nitrite, nitrate, thiocyanate, and isothiocyanate; SO_4^{2-} and O^{2-};

L[2] is CO, H_2O, MeOH, CH_3CN or dimethyl sulfoxide.

In a further embodiment of the invention, in the catalyst of general formula (I), (II) or (III)

NHC is 1-ethyl-3-methylimidazol-2-ylidene (emim), 1-butyl-3-methylimidazol-2-ylidene (bmim); 1-hexyl-3-methylimidazol-2-ylidene (hexmim), 1-benzyl-3-methylimidazol-2-ylidene (Bnmim), or 1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron);

Pws is a Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts), or 1,3,5-triaza-7-phosphadamantane (pta), tetrasulfonated 1,2-bis(diphenylphosphino)ethane (dppets), tetrasulfonated 1,3-bis(diphenylphosphino)propane (dpppts) or a compound of formula (4) below:

 (4),

where m is an integer from 1 to 6,

L[1] is H^-, F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$ (acetate), SO_4^{2-} or O^{2-}; and

L[2] is CO, H_2O, MeOH or CH_3CN or dimethyl sulfoxide.

In a further embodiment of the invention, in the catalyst of general formula (I), (II) or (III)

NHC is 1-ethyl-3-methylimidazol-2-ylidene (emim), 1-butyl-3-methylimidazol-2-ylidene (bmim); 1-hexyl-3-methylimidazol-2-ylidene (hexmim), 1-benzyl-3-methylimidazol-2-ylidene (Bnmim), or 1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron);

Pws is a Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts), or 1,3,5-triaza-7-phosphaadamantane (pta);

L^1 is Cl^-, Br^-, $CH_3CO_2^-$, SO_4^{2-}, or O^{2-}; and

L^2 is CO or H_2O.

In one embodiment of the invention, the catalyst is a catalyst of general formula (I):

$$\mathbf{[M(NHC)_n(Pws)_p(L^1)_q(L^2)_r]}\ (I),$$

wherein

M is selected from non-platinum transition metals and tin, preferably from manganese, iron, cobalt, nickel and copper;

NHC is an N-heterocyclic carbene ligand, preferably selected from the group consisting of: 1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), 1-R^1-3-R^2-imidazol-2-ylidene, 1-R^1-3-R^2-imidazolin-2-ylidene and 1-R^1-3-R^2-benzimidazol-2-ylidene, wherein R^1 and R^2 are each independently a straight or branched chain alkyl group of 1 to 5 carbon atoms or a phenyl group, which is unsubstituted or substituted with an alkyl group of 1 to 6 carbon atoms;

Pws is a water soluble phosphine ligand selected from the group consisting of:

a tertiary phosphine of general formula PR^{1}R^{2}R^3, wherein R^1, R^2 and R^3 are independently a straight or branched chain alkyl group of 1 to 5 carbon atoms or a phenyl group, wherein the alkyl group may be substituted with an OH group or a sulphonato group and the phenyl group may be substituted with an alkyl group of 1 to 6 carbon atoms and/or a sulphonato group, provided that at least one of R^1, R^2 and R^3 carries an OH group or a sulphonato group; or

a diphosphine of general formula R^4_2P-*bridge*-PR^5_2, wherein R^4 and R^5 are independently a straight or branched chain alkyl group of 1 to 5 carbon atoms, or a phenyl group, wherein the alkyl group may be substituted with an OH group or a sulfonato group, and the phenyl group may be substituted with an alkyl group of 1 to 6 carbon atoms or a sulfonato group, wherein PR^4_2 and PR^5_2 may have the same or different meanings, provided that at least one of R^4 and R^5 carries an OH group or a sulphonato group; wherein the *bridge* group is a straight chain alkylene group of 1 to 6 carbon atoms, preferably a methylene, ethylene, propylene, butylene or hexylene group;

L[1] is a negatively charged ligand, preferably selected from the group consisting of: H^-, F^- Cl^-, Br^-, I^-, OH^-, HCO_3^- (hydrogencarbonate), HCO_2^- (formate), $CH_3CO_2^-$ (acetate), $[CH_3COCHCOCH_3]^-$ (acetylacetonate), cyanide, isocyanide, nitrite, nitrate, thiocyanate and isothiocyanate;

L[2] is a neutral (non-ionic) ligand selected from the group consisting of: H_2O, CO (carbonyl); a cycloalkadiene of 5 to 10 ring members, optionally substituted with one or more substituents selected from alkyl groups of 1 to 5 carbon atoms and phenyl groups; a π-donor aromatic hydrocarbon ligand of 6 to 10 carbon atoms; dimethylsulfoxide or acetonitrile; and

n, p, q and r are 0, 1, 2, 3 or 4, provided that n + p is at least 1 and $n + p + q + r \leq 8$; furthermore, if n, p, q and/or r are greater than 1, then **NHC**, **Pws**, **L[1]** and/or **L[2]** may be the same or different, respectively.

For example, in formula (I), the carbene is selected from: (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), 1,3-dimethylimidazol-2-ylidene, 1-ethyl-3-methylimidazol-2-ylidene, 1-methyl-3-propylimidazol-2-ylidene, 1-butyl-3-methylimidazol-2-ylidene, 1-methyl-3-pentylimidazol-2-ylidene, 1,3-diethylimidazol-2-ylidene, 1-ethyl-3-propylimidazol-2-ylidene, 1-ethyl-3-butylimidazol-2-ylidene, 1-ethyl-3-pentylimidazol-2-ylidene, 1,3-dipropylimidazol-2-ylidene, 1-propyl-3-butylimidazol-2-ylidene, 1-propyl-3-pentylimidazol-2-ylidene, 1,3-dibutylimidazol-2-ylidene, 1-butyl-3-pentylimidazol-2-ylidene, 1,3-dipentylimidazol-2-ylidene; 1,3-diizopropylimidazol-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)-imidazol-2-ylidene; 1-methyl-3-phenylimidazol-2-ylidene, 1-ethyl-3-phenylimidazol-2-ylidene, 1-propyl-3-phenylimidazol-2-ylidene, 1-butyl-3-phenylimidazol-2-ylidene, 1-pentyl-3-phenylimidazol-2-ylidene, 1,3-diphenylimidazol-2-ylidene; 1,3-dimethylimidazolin-2-ylidene, 1-methyl-3-ethylimidazolin-2-ylidene, 1-methyl-3-propylimidazolin-2-ylidene, 1-methyl-3-butylimidazolin-2-ylidene, 1-

methyl-3-pentylimidazolin-2-ylidene, 1,3-diethylimidazolin-2-ylidene, 1-ethyl-3-propylimidazolin-2-ylidene, 1-ethyl-3-butylimidazolin-2-ylidene, 1-ethyl-3-pentylimidazolin-2-ylidene, 1,3-dipropylimidazolin-2-ylidene, 1-propyl-3-butylimidazolin-2-ylidene, 1-propyl-3-pentylimidazolin-2-ylidene, 1,3-dibutylimidazolin-2-ylidene, 1-butyl-3-pentylimidazolin-2-ylidene, 1,3-dipentylimidazolin-2-ylidene; 1,3-diizopropylimidazolin-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)-imidazolin-2-ylidene; 1-methyl-3-phenylimidazolin-2-ylidene, 1-ethyl-3-phenylimidazolin-2-ylidene, 1-propyl-3-phenylimidazolin-2-ylidene, 1-butyl-3-phenylimidazolin-2-ylidene, 1-pentyl-3-phenylimidazolin-2-ylidene, 1,3-diphenylimidazolin-2-ylidene; 1,3-dimethylbenzimidazol-2-ylidene, 1-methyl-3-ethylbenzimidazol-2-ylidene, 1-methyl-3-propylbenzimidazol-2-ylidene, 1-methyl-3-butylbenzimidazol-2-ylidene, 1-methyl-3-pentylbenzimidazol-2-ylidene, 1,3-diethylbenzimidazol-2-ylidene, 1-ethyl-3-propylbenzimidazol-2-ylidene, 1-ethyl-3-butylbenzimidazol-2-ylidene, 1-ethyl-3-pentylbenzimidazol-2-ylidene, 1,3-dipropylbenzimidazol-2-ylidene, 1-propyl-3-butylbenzimidazol-2-ylidene, 1-propyl-3-pentylbenzimidazol-2-ylidene, 1,3-dibutylbenzimidazol-2-ylidene, 1-butyl-3-pentylbenzimidazol-2-ylidene, 1,3-dipentylbenzimidazol-2-ylidene; 1,3-diizopropylbenzimidazol-2-ylidene; 1,3-di(2,4,6-trimethylpheny)lbenzimidazol-2-ylidene; 1-methyl-3-phenylbenzimidazol-2-ylidene, 1-ethyl-3-phenylbenzimidazol-2-ylidene, 1-propyl-3-phenylbenzimidazol-2-ylidene, 1-butyl-3-phenylbenzimidazol-2-ylidene, 1-pentyl-3-phenylbenzimidazol-2-ylidene and 1,3-diphenylbenzimidazol-2-ylidene.

In formula (I), **Pws** is, for example, a tertiary phosphine of general formula $PR^1R^2R^3$ selected from: $P(CH_2OH)_3$ [tris(hydroxymethyl)phosphine], Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *ortho* position (*o*tppms, *o*tppds, *o*tppts); Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts); and Li, Na, K or Cs salt of a triphenylphosphine, which is monosulfonated in the *para* position (*p*tppms); or a cyclic tertiary phosphine, preferably 1,3,5-triaza-7-phosphaadamantane (pta).

In formula (I), **Pws** is, for example, a phosphine of general formula R^4_2P-*bridge*-PR^5_2, wherein PR^4_2 and PR^5_2 are independently selected from: $P(CH_2OH)_2$ (bis(hydroxymethyl)phosphino group), PPh_2 (diphenylphosphino group), Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *ortho* position; Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *meta* position;

Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *para* position, or a covalently bonded cyclic tertiary phosphino group, preferably 1,3,5-triaza-7-phosphaadamantane (pta).

In a further embodiment of the catalyst of formula (I), **M** is manganese, iron, cobalt, nickel or copper, **NHC** is 1-ethyl-3-methylimidazol-2-ylidene; **Pws** is the Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts); $\mathbf{L^1}$ is H^-, F^-, Cl^-, Br^-, I^- or $CH_3CO_2^-$ (acetate).

In one embodiment of the invention, the catalyst used is a non-isolated (*in situ* generated) catalyst generated from the use of

a water-soluble salt of a metal **M** and at least 1 equimolar amount of an **NHC** precursor and/or **Pws** ligand with respect to the metal ion,

wherein

M, NHC and **Pws** are as defined above.

In an embodiment of the invention, the **NHC** precursor used to generate the non-isolated catalyst is selected from (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), and salts of 1-R^1-3-R^2-imidazolium, 1-R^1-3-R^2-imidazolinium and 1-R^1-3-R^2-benzimidazolium, wherein R^1 and R^2 are each independently a straight or branched chain alkyl group of 1 to 6 carbon atoms or a benzyl group, or a phenyl group, which is unsubstituted or substituted with an alkyl group of 1 to 6 carbon atoms.

In a further embodiment, the **NHC** precursor is selected from: 1-ethyl-3-methylimidazolium chloride (emimCl); 1-butyl-3-methylimidazolium chloride (bmimCl); 1-hexyl-3-methylimidazolium chloride (hexmimCl), 1-benzyl-3-methylimidazolium chloride (BnmimCl); 1-ethyl-3-methylimidazolium acetate (emimAc); 1-butyl-3-methylimidazolium acetate (bmimAc); 1-hexyl-3-methylimidazolium acetate (hexmimAc) and 1-benzyl-3-methylimidazolium acetate (BnmimAc); or (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron).

In a further embodiment of the invention, the **NHC** precursor used to produce the *in situ* generated catalyst is selected from the group consisting of: 1-ethyl-3-methylimidazolium chloride (emimCl); 1-ethyl-3-methylimidazolium acetate; 1-butyl-3-methylimidazolium

chloride (bmimCl); 1-hexyl-3-methylimidazolium chloride (hexmimCl) and 1-benzyl-3-methylimidazolium chloride (BnmimCl); (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron).

In a further embodiment of the invention, the **NHC** precursor used to prepare the non-isolated catalyst is 1-ethyl-3-methylimidazolium chloride (emimCl); 1-butyl-3-methylimidazolium chloride (bmimCl); 1-hexyl-3-methylimidazolium chloride (hexmimCl) and 1-benzyl-3-methylimidazolium chloride (BnmimCl); 1-ethyl-3-methylimidazolium acetate (emimAc); 1-butyl-3-methylimidazolium acetate (bmimAc); 1-hexyl-3-methylimidazolium acetate (hexmimAc) and 1-benzyl-3-methylimidazolium acetate (BnmimAc); (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron); **Pws** is a Li, Na, K or Cs salts of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts), or 1,3,5-triaza-7-phosphadamantane (pta).

The water-soluble salt of metal **M** used for the preparation of the *in situ* catalyst is a water-soluble salt of the metals defined above. It is obvious to a person skilled in the art that the formation of the complex is generally little affected by the starting salt, furthermore, the presence of strong sigma-donor ligands (**NHC** and/or **Pws**) was found to be a key factor for the invention, therefore, the kind of the anion in the water-soluble salt is not particularly limited, provided that the salt is water-soluble. The latter is necessary because the *in situ* catalyst is formed and applied in an aqueous reaction medium. The selection of suitable metal salts is not difficult for the skilled person. Typical salts are the halide, nitrate, sulphate, acetate, etc. salts of the M metals defined above. Chloride or acetate salts are most commonly used because of their easy availability.

Typical metal salts used include: $NiCl_2 \times 6H_2O$; CuCl; $CuCl_2 \times H_2O$; $FeCl_2 \times 4H_2O$; $FeCl_3 \times nH_2O$; $MnCl_2 \times H_2O$; $CoCl_2$; $LaCl_3 \times 7H_2O$; $TiOSO_4 \times xH_2O \times yH_2SO_4$, NH_4VO_3, $(NH_4)_2MoO_4 \times 4H_2O$, $YCl_3 \times 6H_2O$, $CrCl_3 \times 6H_2O$, $SnCl_2 \times 2H_2O$, [Co(acetate)$_2$]; [Cu(acetate)$_2$]; [Mn(acetate)$_2$]; $NiCO_3$ etc.

For the preparation of the non-isolated catalyst, at least 1 equimolar amount of **NHC** precursor and/or **Pws** ligand per **M** metal ion is used. Typically, no more than 6 ligands are incorporated into the complex, but to facilitate the complexation reaction, a relatively large excess of ligands up to 0-10 equimolar amounts of **NHC** precursor and 0-10 equimolar amounts of **Pws** ligand may be used. However, typically 0-6 equimolar amounts of **NHC**

precursor and 0-6 equimolar amounts of **Pws** ligand are used. In most cases, the **NHC** precursor and/or **Pws** ligand is added in a total of up to 6 equimolar amounts.

In an embodiment of the invention, the non-isolated catalyst is prepared using 0-2 equimolar amounts of **NHC** precursor and/or 0-2 equimolar amounts of **Pws** ligand with respect to metal ion M, with the proviso that the **NHC** precursor and **Pws** ligand are present in total amounts of 1-4 equimolar amounts with respect to metal ion.

It is obvious to the skilled person that, in the case of non-isolated catalysts, the complex or the catalytic unit is formed in the reaction mixture from the metal salts and ligands used, and its exact formula/structure may or may not be known. However, based on the starting materials used, general knowledge and proven catalytic activity, it can be assumed that the complexes formed *in situ* correspond to the general formula (I), (II) or (III).

The isolated or non-isolated catalysts used according to the invention are optionally used with excess ligands, typically excess water-soluble phosphine ligands.

We note that in the case of isolated catalysts, the catalyst defined by formula (I), (II) or (III) refers to the metal complex compound added to the reaction mixture. It is obvious to a person skilled in the art that the exact formula/structure of the catalytic unit (active species) formed in the aqueous medium used may differ depending on the composition of the reaction mixture (e.g. formation of solvate complexes, the conversion of polynuclear starting compounds into mononuclear metal complexes, ligand exchange with an excess of a water-soluble phosphine (Pws), L^1 (ionic) and/or L^2 (neutral) ligand). The formula given for the catalyst can therefore be considered as a precursor of the actual catalytic unit (active species).

It is also noted that certain metals, in particular iron and cobalt, are known to form polynuclear complexes. Polynuclear complexes comprising metals as defined for the catalysts of the invention, in particular iron or cobalt, and at least one strong sigma-donor ligand selected from N-heterocyclic carbene ligands and water-soluble phosphine ligands, also fall within the scope of the invention. These catalysts are defined by general formulae (II) and (III) and are considered to be close analogues of the catalysts characterized by general formula (I).

It is obvious to the skilled person that if Pws is a multidentate ligand, the ligand may be coordinated to the metal atom via one or more P atoms.

We also note that in case of the negative ions (L^1) in the formula of the catalyst, it is not always clear whether the ion is indeed coordinated as a ligand in the complex or whether it is rather considered as a counterion. However, in the context of the present invention, the anions in the formulae in the examples are considered to be L^1 ligands.

The invention further relates to a process for releasing hydrogen gas, wherein the process comprises the decomposition of formate, preferably sodium formate (HCO_2Na), lithium formate (HCO_2Li), cesium formate (HCO_2Cs) and/or potassium formate (HCO_2K) in an aqueous reaction system in the presence of a catalyst as defined above, to produce hydrogen gas free of CO_x by-products.

The process for releasing hydrogen gas is carried out in an oxygen-free atmosphere at elevated temperature, preferably at 60-100°C, more preferably at 60-80°C, at a pH greater than 8, preferably at pH=8.3±0.2.

The invention further relates to a process for storing hydrogen gas, wherein the process comprises hydrogenating hydrogencarbonate (HCO_3^-), preferably sodium hydrogencarbonate ($NaHCO_3$), lithium hydrogencarbonate ($LiHCO_3$), cesium hydrogencarbonate ($CsHCO_3$) and/or potassium hydrogencarbonate ($KHCO_3$) in an aqueous reaction system in the presence of a catalyst as defined above, to produce a formate, preferably sodium formate (HCO_2Na), lithium formate (HCO_2Li), cesium formate (HCO_2Cs) and/or potassium formate (HCO_2K).

The process for storing hydrogen gas is carried out in an oxygen-free atmosphere at elevated temperature, preferably at 60-100°C, more preferably at 80°C, at a H_2 pressure of 1-1200 bar, preferably 10-100 bar, more preferably 30-40 bar, more preferably 30 or 40 bar.

If the catalytic hydrogenation of hydrogencarbonate to formate according to the invention and the catalytic decomposition of formate to hydrogencarbonate according to the invention are combined in such a way that the mentioned steps are carried out in the same reaction system in an aqueous medium in the presence of a water-soluble catalyst, i.e. the reactants and reaction products are formed in a reversible reaction cycle, a hydrogen storage system, preferably a hydrogen accumulator, can be formed.

Accordingly, the invention further relates to a process for releasing and storing hydrogen gas, the process comprising the steps of:

i) decomposition of formate, preferably sodium formate (HCO_2Na), lithium formate (HCO_2Li), cesium formate (HCO_2Cs) and/or potassium formate (HCO_2K) in an aqueous reaction system in the presence of a catalyst as defined above, to produce hydrogen gas (H_2) free of CO_x by-products; and

ii) hydrogenation of the hydrogencarbonate (HCO_3^-), preferably sodium hydrogencarbonate ($NaHCO_3$), lithium hydrogencarbonate ($LiHCO_3$), cesium hydrogencarbonate ($CsHCO_3$) and potassium hydrogencarbonate ($KHCO_3$), produced in step i) in an aqueous reaction system in the presence of the catalyst used in step i), to produce formate, preferably sodium formate (HCO_2Na), lithium formate (HCO_2Li), cesium formate (HCO_2Cs) and/or potassium formate (HCO_2K);

wherein the decomposition of the formate is carried out in an oxygen-free atmosphere at elevated temperature, preferably at 60-100°C, more preferably at 60-80°C, at a pH greater than 8, preferably at pH=8.3±0.2;

and wherein the step of hydrogenation of hydrogencarbonate is carried out in an oxygen-free atmosphere at elevated temperature, preferably at 60-100°C, more preferably at 80°C, at a H_2 pressure of 1-1200 bar, preferably 10-100 bar, more preferably 30-40 bar, more preferably 30 or 40 bar;

and wherein the reactants and reaction products are formed in a reversible reaction cycle using the reaction system of the formate decomposition step and the hydrogencarbonate hydrogenation step, and optionally this reaction cycle is repeated.

Thus, according to an embodiment of our invention, the process for storing hydrogen gas and the process for releasing hydrogen gas are implemented in a single reaction system, a hydrogen storage system.

A hydrogen storage system can be used in such a way that the catalytic hydrogenation of hydrogencarbonate is performed in a hydrogenation reactor near a renewable energy production facility to store energy produced in excess of immediate needs (energy that is not immediately used), and then the formate solution is transported and the hydrogen is released in another facility (either for direct hydrogen use e.g. in chemical reactions, or for the production of electricity, e.g. in a fuel cell). The remaining hydrogencarbonate solution can then be returned to the hydrogenation reactor and re-hydrogenated. In this case, the hydrogen

storage system, although chemically considered to be the same system, is not called a hydrogen accumulator.

According to a more preferred embodiment, said reactions are carried out in the same reaction system and in the same apparatus, in which case said hydrogen storage system is a hydrogen accumulator.

The invention also relates to the use of a hydrogen storage system according to the invention for storing and, if necessary, releasing the hydrogen required for the operation of a fuel cell (or other device requiring H_2).

The methods used to prepare the metal complexes used as catalysts described in this specification are detailed below. The compounds used as starting materials are commercially available.

Preparation method **A**

A-1. Preparation of free carbene

To a solution of the desired NHC chloride (most often emim, bmim, etc.) (2.5051 mmol) in 8 mL of THF - after stirring at room temperature for 15 minutes - 1.09 equivalents of t-BuOK (2.7305 mmol) are added under inert conditions, followed by stirring for an additional 20 minutes. Then the yellowish mixture is filtered through a Hyflo Super-Cel® filter aid.

A-2. Preparation of metal-carbene ($[M(NHC)_n(L^1)_q(L^2)_r]$) complex

A solution of the appropriate amount of metal salt, e.g. M-chloride [*e.g.* $NiCl_2{\times}6H_2O$; $CuCl$; $CuCl_2{\times}H_2O$; $FeCl_2{\times}4H_2O$; $FeCl_3{\times}nH_2O$; $MnCl_2{\times}H_2O$; $CoCl_2$; $LaCl_3{\times}7H_2O$; NH_4VO_3, $(NH_4)_2MoO_4{\times}4H_2O$, $YCl_3{\times}6H_2O$, $CrCl_3{\times}6H_2O$, $SnCl_2{\times}2H_2O$, $TiOSO_4{\times}xH_2O{\times}yH_2SO_4$] (2,5051 mmol) in 5 mL of THF is stirred at 50 °C for 40 min. Simultaneously, the solution of free carbene is prepared as described in **A-1**. (The metal salt and the carbene are in equivalent amounts.) Then the yellow solution of free carbene is added to the solution of metal salt under inert conditions and the reaction mixture is refluxed for 4 hours. After 4 hours, the mixture is cooled. The desired product ($[M(NHC)_n(L^1)_q(L^2)_r]$) is precipitated from the solution and the solution phase is removed by pipette, then the obtained material is washed with diethyl ether and dried under vacuum. If the desired product does not

precipitate from the reaction mixture, the solution is evaporated, washed with diethyl ether, and dried under vacuum.

A-3. Synthesis of metal-carbene-phosphine ($[M(NHC)_n(Pws)_p(L^1)_q(L^2)_r]$) complex

The M-carbene complex obtained in point **A-2.** (50 mg) is dissolved in 8 mL of methanol under inert conditions, then the appropriate amount (1 equivalent) of phosphine compound (Pws: *m*tppms, *m*tppts) is added. The mixture then is stirred at 50°C for 4 hours. After the reaction time has elapsed, the solution is cooled and then evaporated. The obtained catalyst is washed with diethyl ether and dried under vacuum.

It should be noted that step **A-2** above is basically used for the incorporation of the carbene ligand (NHC), and step **A-3** is used for the incorporation of the phosphine ligand (Pws), however, during the reactions, L^1 ionic ligands and L^2 neutral ligands from the components present in the reaction mixture can also be incorporated into the complex (e.g. the anion of the weighed salt or the H_2O molecule of the crystal water in the salt, furthermore the coordinating solvent used itself may remain in the coordination sphere as an anionic or neutral ligand). This consideration applies in the case of the following preparation routes D and E in an analogous manner.

Preparation method **B**

B-1. Preparation of $[Mn(CO)_4Br(NHC)]$

A solution of the appropriate amount of $[Mn(CO)_5Br]$ (2.5051 mmol) in 5 mL of THF is stirred at 50 °C for 40 min. Simultaneously, the solution of free carbene is prepared as described in **A-1**. (The metal salt and the carbene are in 1 equivalent amount.) Then, the yellow solution of free carbene is added to the $[Mn(CO)_5Br]$ solution under inert conditions and the reaction mixture is refluxed for 4 h. After 4 h, the mixture is cooled. The solution is evaporated, washed with diethyl ether, and dried under vacuum.

B-2. Preparation of $[Mn(CO)_{2-3}Br(NHC)(Pws)_{1-2}]$ complex

The $[Mn(CO)_4Br(NHC)]$ complex (1.0281 mmol) prepared according to **B-1.** is dissolved in 15 mL of THF and the appropriate amount of 1 or 2 equivalents of phosphine (Pws: *m*tppms, pta) is added under nitrogen atmosphere. Then it is stirred for 4 hours at 50°C. In case the desired product precipitates from the solution, the solution phase is removed

with a pipette, the solid residue is washed with diethyl ether, and the resulting material is then dried under vacuum. If the product does not precipitate from the reaction mixture, the solution is evaporated, and then it is also washed with diethyl ether, and dried under vacuum.

Preparation method **C**

C-1. Preparation of $[Fe_3(CO)_{11}(NHC)]$

A solution of the appropriate amount of $[Fe_3(CO)_{12}]$ (2.5051 mmol) in 5 mL of THF is stirred at 50 °C for 40 min. Simultaneously, the solution of free carbene is prepared as described in **A-1**. Then, the yellow solution of free carbene is added to the $[Fe_3(CO)_{12}]$ solution in an equivalent amount under inert conditions and the reaction mixture is refluxed for 4 h. After 4 h, the mixture is cooled. The solution is evaporated, washed with diethyl ether, and dried under vacuum.

C-2. Preparation of $[Fe_3(CO)_{10}(NHC)(Pws)]$, $[Fe_3(CO)_9(NHC)(Pws)_2]$ and $[Fe_3(CO)_8(NHC)(Pws)_3]$

The $[Fe_3(CO)_{11}(NHC)]$ complex (0.6629 mmol) prepared according to C-1 is dissolved in 15 mL of THF and the appropriate amount (1 - 3 equivalents) of phosphine (Pws: *m*tppms, pta) is added under nitrogen atmosphere. After that, it is stirred for 4 hours at 50°C. Finally, the solution is cooled and the solid product precipitates during cooling. The solution phase is removed with a pipette, and the resulting material is washed with diethyl ether, and then is dried under vacuum.

Preparation method **D**

D-1. Preparation of Ag-NHC

A solution of 1.30 mmol NHC chloride (NHC: emim, bmim, Bnmim, hexmim) in 10 mL dichloromethane is added to a suspension of 0.65 mmol Ag_2O in 20 mL of dichloromethane at room temperature, and the reaction mixture is stirred at reflux temperature for 3 hours. Almost all amount of the Ag_2O reacts, and a clear solution is formed from the blackish suspension. It is then filtered through Hyflo Super-Cel® filter aid to remove unreacted Ag_2O. The solvent is removed under vacuum and the resulting material is used to prepare the corresponding M-NHC complexes.

D-2. Preparation of metal-carbene ($[M(NHC)_n(L^1)_q(L^2)_r]$) complex

A solution of the metal salt (0.85 mmol) in 0.5 mL of 2-methoxyethanol is added in small portions to a solution of Ag-NHC (0.49 mmol) in 20 mL of dichloromethane prepared according to **D-1**. The resulting reaction mixture is then stirred at reflux temperature for 4 hours. After cooling the reaction mixture, the solution is filtered through Hyflo Super-Cel® filter aid to remove AgCl. The solvent is removed under vacuum. The remaining sticky material is washed with diethyl ether until a solid material is obtained. Finally, the obtained $[M(NHC)_n(L^1)_q(L^2)_r]$ complexes are directly used for the catalytic reactions.

D-3. Synthesis of metal-carbene-phosphine ($[M(NHC)_n(Pws)_p(L^1)_q(L^2)_r]$) complex

The water-soluble phosphine (Pws: *m*tppms, *m*tppts, pta), in an amount equivalent to the metals, is added to the solution of various $[M(NHC)_n(L^1)_q(L^2)_r]$ complexes in methanol prepared according to **D-2.**, and then the resulting solution is stirred for 4 hours at 50°C. After the reaction time, it is filtered through Hyflo Super-Cel® filter aid. The solvent is removed under vacuum. Then, the residue is washed with diethyl ether until a solid material is obtained, and finally dried under vacuum.

Preparation method **E**

E-1. Preparation of $[M(Nitron)(L^1)_q(L^2)_r]$

0.64 mmol of nitron dissolved in 10 mL of acetonitrile is added dropwise to a solution of 0.64 mmol of metal salt [*e.g.* $NiCl_2\times6H_2O$; $CuCl$; $CuCl_2\times H_2O$; $FeCl_2\times4H_2O$; $FeCl_3\times nH_2O$; $MnCl_2\times H_2O$; $CoCl_2$; $LaCl_3\times7H_2O$; $TiOSO_4\times xH_2O\times yH_2SO_4$] in 10 mL of acetonitrile at room temperature. The mixture is then stirred at reflux temperature for 6 hours, and the solvent is then removed under vacuum. The resulting material is washed with diethyl ether and dried under vacuum. The solid material thus obtained ($[M(Nitron)(L^1)_q(L^2)_r]$) is used directly for the catalytic reactions.

E-2. Synthesis of metal-nitron-phosphine ($[M(Nitron)(Pws)_p(L^1)_q(L^2)_r]$) complex

The water-soluble phosphine (Pws: *m*tppms, *m*tppts, pta), in an amount equivalent to the metals, is added to the solution of various $[M(Nitron)(L^1)_q(L^2)_r]$ complexes in methanol prepared according to **E-1.**, and then the resulting solution is stirred for 4 hours at 50°C. After the reaction time, it is filtered through Hyflo Super-Cel® filter aid. The solvent is

removed under vacuum. Then, the residue is washed with diethyl ether until a solid material is obtained, and finally dried under vacuum.

The results of the application of the new catalysts prepared by different methods are summarized in Tables 3-10, in each case, the preparation method of the complex is specified individually, together with its activity.

Examples of embodiments are described below in which catalysts generated *in situ* or prepared and isolated by one of the methods A-E above showed catalytic activity during dehydrogenation and/or hydrogenation in the given reaction system.

EXAMPLES

Description of a general dehydrogenation reaction system:

Reaction conditions: [formate]/[M] = **5-200**; T = **60-80°C**; reaction time = **1-2 h**; V = **2-5 mL**; the amount of converted formate was determined by HPLC, the conversion values in all cases refer to the conversion (consumption) of the starting formate.

The dehydrogenation was always carried out in an oxygen-free atmosphere (in the presence of nitrogen gas). An oxygen-free atmosphere can also be provided, for example, with argon gas. Furthermore, dehydrogenation was always carried out at pH = 8.3±0.2, thus ensuring that we avoid the loss of storage material, which would include decomposition of bicarbonate along with the formation of carbon dioxide, as previously mentioned.

Example 1: Studies of **cobalt** complex catalysts in dehydrogenation.

i. metal salt: [**Co**(acetate)$_2$]; **NHC** precursor: 1-ethyl-3-methylimidazolium chloride; **Pws**: *m*tppts-Na_3

The following were mixed in 3 mL of MeOH at room temperature: 10 mg of [Co(acetate)$_2$]×4H_2O (0.04 mmol), 12 mg of emim(HCl) (0.082 mmol) and 8.5 mg of Na_2CO_3 (0.081 mmol). The resulting solution was stirred for 1 h, after which 62 mg of *m*tppts-Na_3 (2 eq.) was added. During 1 h of stirring, a pinkish-pale purple solution was obtained, from which the solvent was removed under vacuum, 2.0 mL of water and 100 mg of K-formate (1.2

mmol) were added to the residue. Dehydrogenation was carried out at 60°C for 1 h. The experiment was performed 2 times and the conversion achieved was 10-11% by HPLC.

ii. metal salt: [**Co**(acetate)$_2$]; **NHC** precursor: 1-ethyl-3-methylimidazolium chloride

The following were mixed in 2 mL of MeOH at room temperature: 25 mg of [Co(acetate)$_2$]×4H$_2$O (0.1 mmol), 30 mg of emim(HCl) (0.2 mmol) and 21 mg of Na_2CO_3 (0.2 mmol). The resulting solution was stirred for 1 h to give a bluish-pale violet solution from which the solvent was removed under vacuum, 2,0 mL of water and 96 mg of K-formate (1.14 mmol) were added to the residue. The dehydrogenation was carried out at 60 °C for 1 h. The experiment was carried out 2 times and the conversion achieved was 11-13% by HPLC.

iii. metal salt: [**Co**(acetate)$_2$]; **NHC** precursor: 1-ethyl-3-methylimidazolium acetate; **Pws**: *m*tppts-Na_3

The following were mixed in 2 mL of MeOH at room temperature: 30 mg of [Co(acetate)$_2$]×4H$_2$O (0.12 mmol), 40 mg (0.24 mmol) of emim acetate and 140 mg of *m*tppts-Na_3 (0.23 mmol). 25 mg of Na_2CO_3 (0.24 mmol) was added to the resulting pink solution. The resulting solution was stirred for 72 h to give a pink solution with a pale white solid. After filtration, the solvent was removed under vacuum, 2.0 mL of water and 112 mg of K-formate (1.33 mmol) were added to the residue. The dehydrogenation was carried out at 60 °C for 1 hour. The experiment was carried out 5 times and the conversion achieved was 15-22% by HPLC.

iv. metal salt: [**Co**(acetate)$_2$]; **NHC** precursor: 1-ethyl-3-methylimidazolium acetate

The following were mixed in 5 mL of MeOH at room temperature: 20 mg of [Co(acetate)$_2$]×4H$_2$O (0.08 mmol) and 27 mg of emim acetate (0.16 mmol) were mixed. The resulting strong pink solution was stirred for 23 h, and the solvent was removed under vacuum. 2.0 mL of water and 104 mg of K-formate (1.24 mmol) was added to the resulting purple sticky substance (which dissolved). The dehydrogenation was carried out at 60 °C for 1 hour. The experiment was carried out 4 times and the conversion achieved was 6-11% by HPLC.

v. **Systematic studies (Table 3):**

Commonly used reaction conditions: mass of **Co-complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 80°C - all measurements reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%).

Table 3

Co complex (preparation method)	+ ligand			**conversion (%)**
	*m*tppm	*m*tppts	pta	
$[CoCl_2(emim)]$ (**A**)	–	–	–	**7.0**
$[CoCl_2(emim)]$ (**A**)	1 eq.	–	–	**5.65**
$[CoCl_2(emim)]$ (**A**)	–	1 eq.	–	**6.75**
$[CoCl_2(emim)]$ (**A**)	–	2 eq.	–	**6.35**
$[CoCl_2(emim)]$ (**A**)	–	–	1 eq.	**4.65**
$[CoCl_2(bmim)]$ (**A**)	–	–	–	**7.7**
$[CoCl_2(bmim)]$ (**A**)	1 eq.	–	–	**7.8**
$[CoCl_2(bmim)]$ (**A**)	–	1 eq.	–	**10.65**
$[CoCl_2(bmim)]$ (**A**)	–	–	1 eq.	**3.1**
$[CoCl_2(bmim)(mtppms)]$ (**A**)	–	–	–	**9.15**
$[CoCl_2(bmim)(mtppts)]$ (**A**)	–	–	–	**7.0**
$[CoCl_2(Bnmim)]$ (**D**)	–	–	–	**5.0**
$[CoCl_2(Bnmim)]$ (**D**)	–	1 eq.	–	**10.0**
$[CoCl_2(hexmim)]$ (**D**)	–	–	–	**5.5**
$[CoCl_2(hexmim)]$ (**D**)	–	1 eq.	–	**6.5**
$[CoCl_2(hexmim)]$ (**D**)	1 eq.	–	–	**9.0**
$[CoCl_2(hexmim)(mtppms)]$ (**D**)	–	–	–	**4.0**
$[CoCl_2(hexmim)(mtppts)]$ (**D**)	–	–	–	**10.0**
$[CoCl_2(emim)(mtppms)]$ (**A**)	–	–	–	**5.2**
$[CoCl_2(emim)(mtppts)]$ (**A**)	–	–	–	**4.0**
$[CoCl_2(Nitron)]$ (**E**)	–	–	–	**8.0**
$[CoCl_2(Nitron)]$ (**E**)	–	1 eq.	–	**6.0**
$[CoCl_2(Nitron)(mtppts)]$ (**E**)	–	–	–	**8.5**

Example 2: Studies of **copper** complex catalysts in dehydrogenation.

i. metal salt: [**Cu**Cl]; **NHC** precursor: 1-ethyl-3-methylimidazolium acetate; **Pws**: *m*tppts-Na_3

The following were mixed in 2 mL of MeOH at room temperature: 10 mg of [CuCl] (0.1 mmol) and 14 mg of emim acetate (0.08 mmol). 22 mg of Na_2CO_3 (0.21 mmol) was added to the resulting yellowish green solution, and stirred for 1 h to give a yellowish green solution and a yellowish green solid. 62 mg of *m*tppts-Na_3 (0,1 mmol) was added to the solution and stirred for 0.5 hour. The solvent was then removed under vacuum, 2.0 mL of water and 52 mg of K-formate (0.62 mmol) were added to the residue. The dehydrogenation was carried out at 60 °C for 1 hour. The experiment was performed once and the conversion achieved was 8% by HPLC.

ii. metal salt: [**Cu**$(acetate)_2$]; **NHC** precursor: 1-ethyl-3-methylimidazolium chloride; **Pws**: *m*tppts-Na_3

The following were mixed in 2 mL of water: 10 mg of [$Cu(acetate)_2$] (0.055 mmol) and 90 mg of *m*tppts-Na_3 (0.144 mmol) to give a pale green solution. $NaBH_4$ solution (5 eq.) was slowly added dropwise to the resulting solution while cooling with ice. The resulting solution was stirred for 1 hour to give a peach-flower coloured solution to which 20 mg of emim(HCl) (0.136 mmol) was added. After stirring for 0.5 h, 100 mg of K-formate (1.2 mmol) was added. The dehydrogenation was carried out at 60°C for 1 hour. The experiment was carried out 2 times and the conversion achieved was 3-5% by HPLC.

iii. metal salt: [**Cu**$(acetate)_2$]; **Pws**: *m*tppts-Na_3

The following were mixed in 2 mL of water: 10 mg of $Cu(acetate)_2$ (0.055 mmol) and 90 mg of *m*tppts-Na_3 (0.144 mmol) to give a pale green solution to which 100 mg of K-formate (1.2 mmol) was added. The dehydrogenation was carried out at 60°C for 1 hour. The experiment was carried out 2 times and the conversion achieved was 20% by HPLC.

iv. Systematic studies (Table 4):

Commonly used reaction conditions: mass of **Cu(I) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 60°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%).

Table 4

Cu complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[CuCl(emim)] (**A,D**)	–	–	–	**4.5**
[CuCl(emim)] (**A,D**)	1 eq.	–	–	**9.5**
[CuCl(emim)] (**A,D**)	–	1 eq.	–	**9.4**
[CuCl(emim)] (**A,D**)	–	–	1 eq.	**6.4**
[CuCl(emim)(*m*tppms)] (**A,D**)	–	–	–	**5.3**
[CuCl(emim)(*m*tppts)] (**A,D**)	–	–	–	**4.1**
[CuCl(bmim)] (**A,D**)	–	–	–	**7.9**
[CuCl(bmim)] (**A,D**)	1 eq.	–	–	**5.2**
[CuCl(bmim)] (**A,D**)	–	1 eq.	–	**12**
[CuCl(bmim)(*m*tppms)] (**A,D**)	–	–	–	**4.5**
[CuCl(bmim)(*m*tppts)] (**A,D**)	–	–	–	**5**
[CuCl(hexmim)(*m*tppts)] (**D**)	–	–	–	**3**
[CuCl(Nitron)] (**E**)	–	–	–	**6.5**
[CuCl(Nitron)] (**E**)	1 eq.	–	–	**8**
[CuCl(Nitron)] (**E**)	–	1 eq.	–	**2**
[CuCl(Nitron)] (**E**)	–	–	1 eq.	**3**
[CuCl(Nitron)(*m*tppts)] (**E**)	–	–	–	**9**

v. Systematic studies (Table 5):

Commonly used reaction conditions: mass of **Cu(II) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 60°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%)

Table 5

Cu complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[$CuCl_2$(emim)] (**A**)	–	–	–	**5.65**
[$CuCl_2$(emim)] (**A**)	1 eq.	–	–	**5.6**
[$CuCl_2$(emim)] (**A**)	–	1 eq.	–	**9.8**
[$CuCl_2$(emim)] (**A**)	–	–	1 eq.	**9.4**
[$CuCl_2$(emim)(*m*tppms)] (**A**)	–	–	–	**7.95**
[$CuCl_2$(emim)(*m*tppts)] (**A**)	–	–	–	**8.96**
[$CuCl_2$(bmim)] (**A,D**)	–	–	–	**6.3**
[$CuCl_2$(bmim)] (**A**)	1 eq.	–	–	**12.1**
[$CuCl_2$(bmim)] (**A**)	–	1 eq.	–	**7.8**
[$CuCl_2$(bmim)] (**A**)	–	–	1 eq.	**9**
[$CuCl_2$(bmim)(*m*tppms)] (**A**)	–	–	–	**3.4**
[$CuCl_2$(bmim)(*m*tppts)] (**A,D**)	–	–	–	**9.25**
[$CuCl_2$(hexmim)(*m*tppts)] (**D**)	–	–	–	**3**
[$CuCl_2$(hexmim)(*m*tppts)] (**D**)	–	1 eq.	–	**1**

Example 3: Studies of nickel complex catalysts in dehydrogenation

i. Systematic studies (Table 6):

Commonly used reaction conditions: mass of **Ni(II) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 60°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%)

Table 6

Ni complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[$NiCl_2$(emim)] (**A**)	–	–	–	**8.7**
[$NiCl_2$(emim)] (**A**)	1 eq.	–	–	**3.4**
[$NiCl_2$(emim)] (**A**)	–	1 eq.	–	**6.9**
[$NiCl_2$(emim)] (**A**)	–	–	1 eq.	**7.25**
[$NiCl_2$(emim)(*m*tppms)] (**A**)	–	–	–	**6.6**

Ni complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[$NiCl_2$(emim)(*m*tppts)] (**A**)	–	–	–	**7.6**
[$NiCl_2$(bmim)] (**A**)	–	–	–	**5.2**
[$NiCl_2$(bmim)] (**A**)	1 eq.	–	–	**7**
[$NiCl_2$(bmim)] (**A**)	–	1 eq.	–	**7.8**
[$NiCl_2$(bmim)(*m*tppms)] (**A**)	–	–	–	**8.2**
[$NiCl_2$(bmim)(*m*tppts)] (**A**)	–	–	–	**10.9**
[$NiCl_2$(Bnmim)] (**D**)	–	–	–	**10.9**
[$NiCl_2$(Bnmim)] (**D**)	1 eq.	–	–	**12.0**
[$NiCl_2$(hexmim)] (**D**)	–	–	–	**4.0**
[$NiCl_2$(hexmim)(*m*tppms)] (**D**)	–	–	–	**4.0**
[$NiCl_2$(hexmim)(*m*tppts)] (**D**)	–	–	–	**9.0**
[$NiCl_2$(Nitron)] (**E**)	–	–	–	**9.0**
[$NiCl_2$(Nitron)] (**E**)	1 eq.	–	–	**10.0**
[$NiCl_2$(Nitron)] (**E**)	–	1 eq.	–	**8.0**
[$NiCl_2$(Nitron)] (**E**)	–	–	1 eq.	**12.0**

Example 4: Studies of manganese complex catalysts in dehydrogenation.

i. metal salt: [**Mn**(acetate)$_2$]; **NHC** precursor: 1-ethyl-3-methylimidazolium acetate

The following were mixed in 2 mL MeOH at room temperature: 23 mg of [Mn(acetate)$_2$] (0.13 mmol) and 46 mg of emim acetate (0.27 mmol) to give a colourless solution to which 28 mg of Na_2CO_3 (0.26 mmol) was added. The solution was stirred for 20 h to give a pale yellow/brown solution and a pale brown solid. After filtration, the solvent was removed under vacuum. 2.0 mL of water and 121 mg of K-formate (1.44 mmol) was added to the residue. The dehydrogenation was carried out at 60°C for 1 hour. The experiment was performed 2 times and the conversion achieved was 14-15% by HPLC.

ii. metal salt: [**Mn**(acetate)$_2$]; **Pws**: *m*tppts-Na_3

The following were mixed in 7 mL of water: 17 mg of [Mn(acetate)$_2$] (0.1 mmol) and 380 mg of *m*tppts-Na$_3$ (0.6 mmol) to give a pale yellow solution. NaBH$_4$ solution (3 eq.) was slowly added dropwise to the solution while cooling with ice. The resulting solution was stirred for 2 hours (yellow solution). 115 mg of K-formate (1.37 mmol) was added to the resulting solution. The dehydrogenation was carried out at 60 °C for 1 hour. The conversion achieved was 55% by HPLC.

iii. metal salt: [**Mn**(acetate)$_2$]; **NHC** precursor: 1-ethyl-3-methylimidazolium chloride; **Pws**: *m*tppts-Na$_3$

The following were mixed in 7 mL of water, 17 mg of [Mn(acetate)$_2$] (0.1 mmol) and 380 mg of *m*tppts-Na$_3$ (0.6 mmol) to give a pale yellow solution. NaBH$_4$ solution (3 eq.) was slowly added dropwise to the solution while cooling with ice. The resulting solution was stirred for 2 hours (yellow solution). 132 mg of emim(HCl) (0.9 mmol) was added to the resulting solution (the colour of the solution did not change). 115 mg of K-formate (1.37 mmol) was added to the solution. The dehydrogenation was carried out at 60°C for 1 hour. The conversion achieved was 25% by HPLC.

iv. metal salt: [**Mn**(acetate)$_2$]; **NHC** precursor: 1-ethyl-3-methylimidazolium acetate; **Pws**: *m*tppts-Na$_3$

The following were mixed in 4 mL of MeOH: 36 mg of [Mn(acetate)$_2$] (0.21 mmol), 70 mg of emim acetate (0.41 mmol) and 320 mg of *m*tppts-Na$_3$ (0.51 mmol), to give a yellowish solution to which 44 mg of Na$_2$CO$_3$ (0.42 mmol) was added. The solution was stirred at room temperature for 20 hours to give a pale yellow solution and an off-white solid. After filtration, the solvent was removed under vacuum to give a brown sticky substance to which 2.0 mL of water (clear yellowish solution was obtained) and 108 mg of K-formate (1.29 mmol) were added. The dehydrogenation was carried out at 60 °C for 1 h. The conversion achieved was 10% by HPLC.

v metal complex: [**Mn**Cl$_2$(*m*tppms-Na)$_2$]

15 mg of the previously prepared [MnCl$_2$(*m*tppms-Na)$_2$] complex (0.016 mmol) was dissolved in 2 mL of water to give a colourless clear solution. 27 mg of K-formate (0.32 mmol) was added to the solution. The dehydrogenation was carried out at 60°C for 2 h. The experiment was performed 2 times and the conversion achieved was 2-3% by HPLC.

vi. Systematic studies (Table 7):

Commonly used reaction conditions: mass of **Mn(II) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 60°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%).

Table 7

Mn complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[$MnCl_2$(emim)] (**A,D**)	–	–	–	**7.5**
[$MnCl_2$(emim)] (**A,D**)	1 eq.	–	–	**7**
[$MnCl_2$(emim)] (**A,D**)	–	1 eq.	–	**13.5**
[$MnCl_2$(emim)] (**A,D**)	–	–	1 eq.	**8.35**
[$MnCl_2$(emim)(*m*tppms)] (**A,D**)	–	–	–	**7.9**
[$MnCl_2$(emim)(*m*tppts)] (**A,D**)	–	–	–	**13.2**
[$MnCl_2$(bmim)] (**A,D**)	–	–	–	**7**
[$MnCl_2$(bmim)] (**A,D**)	1 eq.	–	–	**6.7**
[$MnCl_2$(bmim)] (**A,D**)	–	1 eq.	–	**9.8**
[$MnCl_2$(bmim)(*m*tppms)] (**A,D**)	–	–	–	**6.6**
[$MnCl_2$(bmim)(*m*tppts)] (**A,D**)	–	–	–	**9.8**
[$MnCl_2$(Nitron)] (**E**)	–	-	-	**5**
[$MnCl_2$(Nitron)] (**E**)	1 eq.	–	–	**4**
[$MnCl_2$(Nitron)] (**E**)	–	1 eq.	–	**10**
[$MnCl_2$(Nitron)(*m*tppms)] (**E**)	–	–	–	**8**
[$MnCl_2$(Bnmim)(*m*tppms)] (**D**)	–	–	–	**5** (**8** / 80°C)
[$MnCl_2$(hexmim)(*m*tppts)] (**D**)	–	–	–	**9.5** (**8.5** / 80°C)
[$MnCl_2$(hexmim)(*m*tppts)] (**D**)	–	1 eq.	–	**3** (**8** / 80°C)

vii. Systematic studies (Table 8):

Commonly used reaction conditions: mass of **Mn(I) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 80°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%).

Table 8

Mn complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[MnBr(CO)$_4$(emim)] (**B**)	–	–	–	**8.5**
[MnBr(CO)$_3$(emim)(*m*tppms)] (**B**)	–	–	–	**5**
[MnBr(CO)$_3$(emim)(*m*tppms)] (**B**)	1 eq.	–	–	**3.2**
[MnBr(CO)$_3$(emim)(*m*tppms)] (**B**)	2 eq.	–	–	**11.3**
[MnBr(CO)$_3$(emim)(*m*tppms)] (**B**)	3 eq.	–	–	**4.2**
[MnBr(CO)$_3$(emim)(*m*tppms)] (**B**)	–	1 eq.	–	**5.6**
[MnBr(CO)$_3$(emim)(*m*tppms)] (**B**)	–	2 eq.	–	**11.2**
[MnBr(CO)$_3$(emim)(*m*tppms)] (**B**)	–	3 eq.	–	**3.7**
[MnBr(CO)$_3$(emim)(pta)] (**B**)	–	–	–	**11.05**
[MnBr(CO)$_3$(emim)(pta)] (**B**)	1 eq.	–	–	**11.4**
[MnBr(CO)$_3$(emim)(pta)] (**B**)	–	–	1 eq.	**11.2**
[MnBr(CO)$_3$(emim)(pta)] (**B**)	–	–	2 eq.	**11.1**
[MnBr(CO)$_3$(emim)(pta)] (**B**)	–	–	3 eq.	**10.5**
[MnBr(CO)$_2$(emim)(*m*tppms)$_2$] (**B**)	–	–	–	**4.4**
[MnBr(CO)$_2$(emim)(*m*tppms)$_2$] (**B**)	1 eq.	–	–	**8.5**
[MnBr(CO)$_2$(emim)(*m*tppms)$_2$] (**B**)	2 eq.	–	–	**8.2**
[MnBr(CO)$_2$(emim)(*m*tppms)$_2$] (**B**)	3 eq.	–	–	**6.3**
[MnBr(CO)$_2$(emim)(*m*tppms)$_2$] (**B**)	–	1 eq.	–	**8.3**
[MnBr(CO)$_2$(emim)(*m*tppms)$_2$] (**B**)	–	2 eq.	–	**5.9**
[MnBr(CO)$_2$(emim)(*m*tppms)$_2$] (**B**)	–	3 eq.	–	**8**
[MnBr(CO)$_2$(emim)(pta)$_2$] (**B**)	–	–	–	**9.85**
[MnBr(CO)$_2$(emim)(pta)$_2$] (**B**)	–	–	1 eq.	**9.5**
[MnBr(CO)$_2$(emim)(pta)$_2$] (**B**)	–	–	2 eq.	**10.75**

Example 5: Studies of iron complex catalysts in dehydrogenation.

i. Systematic studies (Table 9):

Commonly used reaction conditions: mass of **Fe(II) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 60°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achiebed (standard deviation is ± 0.5%).

Table 9

Fe complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[$FeCl_2$(emim)] (**A,D**)	–	–	–	**5.7**
[$FeCl_2$(emim)] (**A,D**)	1 eq.	–	–	**8.4**
[$FeCl_2$(emim)] (**A,D**)	–	1 eq.	–	**12**
[$FeCl_2$(emim)] (**A,D**))	–	–	1 eq.	**8**
[$FeCl_2$(emim)(*m*tppms)] (**A,D**)	–	–	–	**17.5**
[$FeCl_2$(emim)(*m*tppts)] (**A,D**)	–	–	–	**6**
[$FeCl_2$(bmim)] (**A,D**)	–	–	–	**7.65**
[$FeCl_2$(bmim)] (**A,D**)	1 eq.	–	–	**9.2**
[$FeCl_2$(bmim)] (**A,D**)	–	1 eq.	–	**12.5**
[$FeCl_2$(bmim)(*m*tppms)] (**A,D**)	–	–	–	**2.5**
[$FeCl_2$(bmim)(*m*tppts)] (**A,D**)	–	–	–	**5.05**
[$FeCl_2$(Nitron)] (**E**)	–	–	–	**8.5**
[$FeCl_2$(Nitron)] (**E**)	1 eq.	–	–	**4**
[$FeCl_2$(Nitron)] (**E**)	–	1 eq.	–	**15**
[$FeCl_2$(Bnmim)] (**D**)	–	–	–	**8**
[$FeCl_2$(Bnmim)(*m*tppms)] (**D**)	–	–	–	**7.5**
[$FeCl_2$(Bnmim)(*m*tppms)] (**D**)	1 eq.	–	–	**3**
[$FeCl_2$(Bnmim)(*m*tppms)] (**D**)	2 eq.			**5.5**
[$FeCl_2$(hexmim)(*m*tppts)] (**D**)	–	–	–	**7.5**
[$FeCl_2$(hexmim)(*m*tppts)] (**D**)	–	1 eq.	–	**3**

ii. Systematic studies (Table 10):

Commonly used reaction conditions: mass of **Fe(0) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 60°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%).

Table 10

Fe complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
$[Fe_3(emim)(mtppms)(CO)_{10}]$ (**C**)	–	–	–	**5.3**
$[Fe_3(emim)(mtppms)(CO)_{10}]$ (**C**)	1 eq.	–	–	**7.7**
$[Fe_3(emim)(mtppms)(CO)_{10}]$ (**C**)	–	1 eq.	–	**4.75**
$[Fe_3(emim)(mtppms)(CO)_{10}]$ (**C**)	–	–	1 eq.	**6**
$[Fe_3(emim)(mtppms)_2(CO)_9]$ (**C**)	–	–	–	**8.2**
$[Fe_3(emim)(mtppms)_2(CO)_9]$ (**C**)	1 eq.	–	–	**1.3**
$[Fe_3(emim)(mtppms)_3(CO)_8]$ (**C**)	–	–	–	**6.6**
$[Fe_3(emim)(pta)(CO)_{10}]$ (**C**)	–	–	–	**4.8**
$[Fe_3(emim)(pta)_2(CO)_9]$ (**C**)	–	–	–	**4.05**
$[Fe_3(emim)(pta)_2(CO)_9]$ (**C**)	–	–	1 eq.	**0**

Example 6: Studies of lanthanum complex catalysts in dehydrogenation.

i. Systematic studies (Table 11):

Commonly used reaction conditions: mass of **La(III) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 60°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%).

Table 11

La complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
$[LaCl_3(emim)]$ (**A**)	–	–	–	**23.4**
$[LaCl_3(emim)]$ (**A**)	1 eq.	–	–	**5.45**
$[LaCl_3(emim)]$ (**A**)	–	1 eq.	–	**21.15**
$[LaCl_3(emim)]$ (**A**)	–	–	1 eq.	**18.9**
$[LaCl_3(emim)(mtppms)]$ (**A**)	–	–	–	**3.75**
$[LaCl_3(emim)(mtppts)]$ (**A**)	–	–	–	**7.35**
$[LaCl_3(bmim)]$ (**A**)	–	–	–	**20.4**

La complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[$LaCl_3$(bmim)] (**A**)	1 eq.	–	–	**11.15**
[$LaCl_3$(bmim)] (**A**)	–	1 eq.	–	**16.65**
[$LaCl_3$(bmim)] (**A**)	–	–	1 eq.	**19.3**
[$LaCl_3$(bmim)(*m*tppms)] (**A**)	–	–	–	**6.5**
[$LaCl_3$(bmim)(*m*tppts)] (**A**)	–	–	–	**9.3**
[$LaCl_3$(Nitron)] (**E**)	–	–	–	**12.5**
[$LaCl_3$(Nitron)] (**E**)	1 eq.	–	–	**9.0**
[$LaCl_3$(Nitron)] (**E**)	–	1 eq.	–	**6.1**

Example 7: Studies of titanium complex catalysts in dehydrogenation.

i. Systematic studies (Table 12):

Commonly used reaction conditions: mass of **Ti(IV) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 80°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions obtained (standard deviation is ± 0.5%).

Table 12

Ti complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[$TiOSO_4$(emim)] (**A**)	–	–	–	**10.4**
[$TiOSO_4$(emim)] (**A**)	1 eq.	–	–	**7.61**
[$TiOSO_4$(emim)] (**A**)	–	1 eq.	–	**8.85**
[$TiOSO_4$(emim)] (**A**)	–	–	1 eq.	**4**
[$TiOSO_4$(emim)(*m*tppms)] (**A**)	–	–	–	**6.1**
[$TiOSO_4$(emim)(*m*tppts)] (**A**)	–	–	–	**6.85**
[$TiOSO_4$(bmim)] (**A**)	–	–	–	**6.75**
[$TiOSO_4$(bmim)] (**A**)	1 eq.	–	–	**8.14**
[$TiOSO_4$(bmim)] (**A**)	–	1 eq.	–	**15.4**
[$TiOSO_4$(bmim)] (**A**)	–	–	1 eq.	**6.0**
[$TiOSO_4$(bmim)(*m*tppms)] (**A**)	–	–	–	**7.8**

Ti complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[$TiOSO_4$(bmim)(*m*tppts)] (**A**)	–	–	–	**5.4**
[$TiOSO_4$(Nitron)] (**E**)	–	–	–	**10.0**
[$TiOSO_4$(Nitron)] (**E**)	–	1 eq.	–	**14.0**

Example 8: Studies of tin complex catalysts in dehydrogenation.

i. Systematic studies (Table 13):

Commonly used reaction conditions: mass of **Sn(II) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 80°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%).

Table 13

Sn complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[$SnCl_2$(emim)] (**A**)	–	–	–	**6.4**
[$SnCl_2$(emim)] (**A**)	1 eq.	–	–	**7.7**
[$SnCl_2$(emim)] (**A**)	–	1 eq.	–	**6.55**
[$SnCl_2$(emim)] (**A**)	–	–	1 eq.	**3.35**
[$SnCl_2$(emim)(*m*tppms)] (**A**)	–	–	–	**2.85**
[$SnCl_2$(emim)(*m*tppts)] (**A**)	–	–	–	**7.85**
[$SnCl_2$(bmim)] (**A**)	–	–	–	**7.26**
[$SnCl_2$(bmim)] (**A**)	1 eq.	–	–	**6.3**
[$SnCl_2$(bmim)] (**A**)	–	1 eq.	–	**4.75**
[$SnCl_2$(bmim)] (**A**)	–	–	1 eq.	**6.7**
[$SnCl_2$(bmim)(*m*tppms)] (**A**)	–	–	–	**11.5**
[$SnCl_2$(bmim)(*m*tppts)] (**A**)	–	–	–	**10.3**
[$SnCl_2$(Nitron)] (**E**)	–	–	–	**6.0**
[$SnCl_2$(Nitron)] (**E**)	1 eq.	–	–	**8.0**
[$SnCl_2$(Nitron)] (**E**)	–	1 eq.	–	**9.0**

Example 9: Studies of vanadium complex catalysts in dehydrogenation.

i. Systematic studies (Table 14):

Commonly used reaction conditions: mass of **V(V) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 80°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%).

Table 14

V complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
$[VO_3(emim)]$ (**A**)	–	–	–	**6.9**
$[VO_3(emim)]$ (**A**)	1 eq.	–	–	**2.0**
$[VO_3(emim)(mtppms)]$ (**A**)	–	–	–	**4.95**
$[VO_3(emim)(mtppts)]$ (**A**)	–	–	–	**5.2**
$[VO_3(Nitron)]$ (**E**)	–	–	–	**6.0**
$[VO_3(Nitron)]$ (**E**)	1 eq.	–	–	**8.0**
$[VO_3(Nitron)]$ (**E**)	–	1 eq.	–	**10.0**
$[VO_3(Nitron)]$ (**E**)	–	–	1 eq.	**5.0**

Example 10: Studies of chromium complex catalysts during dehydrogenation.

i. Systematic studies (Table 15):

Commonly used reaction conditions: mass of **Cr(III) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 80°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%).

Table 15

Cr complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
$[CrCl_3(emim)]$ (**A**)	–	–	–	**13.8**
$[CrCl_3(emim)]$ (**A**)	1 eq.	–	–	**12.5**
$[CrCl_3(emim)]$ (**A**)	–	1 eq.	–	**12.2**

[$CrCl_3$(emim)] (**A**)	–	–	1 eq.	**8.0**
[$CrCl_3$(emim)(*m*tppms)] (**A**)	–	–	–	**10.8**
[$CrCl_3$(emim)(*m*tppts)] (**A**)	–	–	–	**7.0**
[$CrCl_3$(bmim)] (**A**)	–	–	–	**15.6**
[$CrCl_3$(bmim)] (**A**)	1 eq.	–	–	**16.0**
[$CrCl_3$(bmim)] (**A**)	–	1 eq.	–	**13.95**
[$CrCl_3$(bmim)] (**A**)	–	–	1 eq.	**10.2**
[$CrCl_3$(bmim)(*m*tppms)] (**A**)	–	–	–	**9.25**
[$CrCl_3$(bmim)(*m*tppts)] (**A**)	–	–	–	**7.4**
[$CrCl_3$(Nitron)] (**E**)	–	–	–	**12.0**
[$CrCl_3$(Nitron)] (**E**)	1 eq.	–	–	**10.0**
[$CrCl_3$(Nitron)] (**E**)	–	1 eq.	–	**10.5**

Example 11: Studies of yttrium complex catalysts in dehydrogenation.

i. Systematic studies (Table 16):

Commonly used reaction conditions: mass of **Y(III) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 80°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation is ± 0.5%).

Table 16

Y complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[YCl_3(emim)] (**A**)	–	–	–	**7.4**
[YCl_3(emim)] (**A**)	1 eq.	–	–	**10.5**
[YCl_3(emim)] (**A**)	–	1 eq.	–	**7.6**
[YCl_3(emim)] (**A**)	–	–	1 eq.	**8.1**
[YCl_3(emim)(*m*tppms)] (**A**)	–	–	–	**5.3**
[YCl_3(emim)(*m*tppts)] (**A**)	–	–	–	**8.7**
[YCl_3(bmim)] (**A**)	–	–	–	**11.4**
[YCl_3(bmim)] (**A**)	1 eq.	–	–	**10.3**

[YCl_3(bmim)] (**A**)	–	1 eq.	–	**10.9**
[YCl_3(bmim)] (**A**)	–	–	1 eq.	**12.9**
[YCl_3(bmim)(*m*tppms)] (**A**)	–	–	–	**7.8**
[YCl_3(bmim)(*m*tppts)] (**A**)	–	–	–	**10.0**
[YCl_3(Nitron)] (**E**)	–	–	–	**8.0**
[YCl_3(Nitron)] (**E**)	1 eq.	–	–	**9.0**
[YCl_3(Nitron)] (**E**)	–	1 eq.	–	**6.0**
[YCl_3(Nitron)] (**E**)	–	–	1 eq.	**9.0**

Example 12: Studies of molybdenum complex catalysts in dehydrogenation.

i. Systematic studies (Table 17):

Commonly used reaction conditions: mass of **Mo(VI) complex** 10 mg; 25 mg of K-formate; 2.0 mL of water; reaction time 2 h; temperature 80°C - all measurements are reproduced 2-3 times, the table shows the average of the conversions achieved (standard deviation ± 0.5%).

Table 17

Mo complex	+ ligand			**conversion (%)**
	*m*tppms	*m*tppts	pta	
[MoO_4(emim)] (**A**)	–	–	–	**14.3**
[MoO_4(emim)] (**A**)	1 eq.	–	–	**5.3**
[MoO_4(emim)] (**A**)	–	1 eq.	–	**6.6**
[MoO_4(emim)] (**A**)	–	–	1 eq.	**2.3**
[MoO_4(emim)(*m*tppms)] (**A**)	–	–	–	**7.1**
[MoO_4(emim)(*m*tppts)] (**A**)	–	–	–	**5.9**
[MoO_4(bmim)] (**A**)	–	–	–	**10.8**
[MoO_4(bmim)] (**A**)	1 eq.	–	–	**5.1**
[MoO_4(bmim)] (**A**)	–	1 eq.	–	**7.0**
[MoO_4(bmim)] (**A**)	–	–	1 eq.	**12.5**
[MoO_4(bmim)(*m*tppms)] (**A**)	–	–	–	**8.1**
[MoO_4(bmim)(*m*tppts)] (**A**)	–	–	–	**5.65**

$[MoO_4(Nitron)]$ (**E**)	–	–	–	**11.0**
$[MoO_4(Nitron)]$ (**E**)	1 eq.	–	–	**8.0**
$[MoO_4(Nitron)]$ (**E**)	–	1 eq.	–	**9.0**
$[MoO_4(Nitron)]$ (**E**)	–	–	1 eq.	**11.0**

Description of a general hydrogenation reaction system:

Reaction conditions: [bicarbonate]/[M] = **20-100**; T = **80°C**; $p(H_2)$ = **30** or **40 bar**; volume of solution used V = **20 mL**; the amount of formate formed in the reaction mixture was determined by HPLC, expressed in concentration (**mM**; for undiluted reaction mixture).

The hydrogenation was always carried out in an oxygen-free atmosphere (in the presence of nitrogen gas). Furthermore, the hydrogenation was always carried out at pH = 8.3±0.2.

Example 13: Studies of cobalt complex catalysts in hydrogenation.

i. metal salt: [**Co**(acetate)$_2$]; **NHC** precursor: 1-ethyl-3-methylimidazolium acetate; **Pws**: *m*tppts-Na_3

The following were mixed in 2 mL of MeOH at room temperature: 30 mg of [Co(acetate)$_2$]×4H_2O (0.12 mmol), 40 mg of emim acetate (0.24 mmol) and 140 mg of *m*tppts-Na_3 (0.23 mmol). 25 mg of Na_2CO_3 (0.24 mmol) was added to the resulting pink solution. The resulting solution was stirred for 72 h to give a pink solution with a pale white solid. After filtration, the solvent was removed under vacuum. The evaporated Co complex, 20.0 mL of H_2O and later 200 mg of K-hydrogencarbonate (2.0 mmol) were added to a 100 mL reactor. The hydrogenation was carried out at 80°C under 40 bar H_2 pressure. By HPLC, 3 mM and 4 mM of formate were obtained after 1 h and 2 h reaction time, respectively.

ii. metal complex: [**Co**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] (**A**);

10 mg of [**Co**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.56 mM of formate was obtained after 4 h reaction time.

iii. metal complex: [**Co**Cl_2(1-butyl-3-methylimidazol-2-ylidene)] (**A**);

10 mg of [**Co**Cl_2(1-butyl-3-methylimidazol-2-ylidene)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.72 mM and 1.09 mM of formate were obtained after 2 h and 65 h reaction time, respectively.

iv. metal complex: [**Co**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**);

7 mg of [**Co**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.9 mM of formate was obtained after 2 h reaction time.

v. metal complex: [**Co**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**);

20 mg of [**Co**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 1.24 mM of formate was obtained after 65 h reaction time.

vi. metal complex: [**Co**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**);

20 mg of [**Co**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.18 mM and 0.26 mM of formate were obtained after 4 h and 17 h reaction time, respectively.

vii. metal complex: [**Co**Cl_2(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] (**E**)

30 mg of previously prepared [$CoCl_2$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The

hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.2252 mM of formate was obtained in 25 h.

Example 14: Studies of copper complex catalysts in hydrogenation.

i. metal salt: [**Cu**Cl]; **Pws**: *m*tppts-Na_3

10 mg of CuCl (0.1 mmol) and 80 mg of *m*tppts-Na_3 (0.13 mmol) were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 40 bar H_2 pressure. By HPLC, 1.4 mM, 2.3 mM and 3.4 mM of formate were obtained after 1 h, 2 h and 4 h reaction time, respectively.

ii. metal complex: [**Cu**Cl(1-ethyl-3-methylimidazol-2-ylidene)] (**A**);

40 mg of [**Cu**Cl(1-ethyl-3-methylimidazol-2-ylidene)] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.32 mM of formate was obtained after 21 h reaction time.

iii. metal complex: [**Cu**Cl(1-ethyl-3-methylimidazol-2-ylidene)] (**A**); **Pws**: *m*tppts-Na_3

20 mg of [**Cu**Cl(1-ethyl-3-methylimidazol-2-ylidene)] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 2.62 mM of formate was obtained after 20 h reaction time.

iv. metal complex: [**Cu**Cl(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**);

10 mg of [**Cu**Cl(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.5 mM of formate was obtained after 2 h reaction time.

v. metal complex: [**Cu**Cl(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**); **Pws**: *m*tppts-Na_3

10 mg of [**Cu**Cl(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] and 10 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.2 mM of formate was obtained after 19 h reaction time.

vi. metal complex: [**Cu**Cl(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**);

10 mg of [**Cu**Cl(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.4 mM, 1.05 mM and 3.94 mM of formate were obtained after 2 h, 3 h and 17 h reaction time, respectively.

vii. metal complex: [**Cu**Cl(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**); **Pws**: *m*tppts-Na_3

10 mg of [**Cu**Cl(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] and 10 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.23 mM, 0.36 mM and 0.57 mM of formate were obtained after 2 h, 3 h and 17 h reaction time, respectively.

viii. metal complex: [**Cu**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**);

20 mg of [**Cu**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.34 mM of formate was obtained after 18 h reaction time.

ix. metal complex: [**Cu**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**);

40 mg of [**Cu**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.14 mM of formate was obtained after 18 h reaction time.

x. metal complex: [**Cu**Cl_2(1-butyl-3-methylimidazol-2-ylidene)] (**A**);

23 mg of [**Cu**Cl_2(1-butyl-3-methylimidazol-2-ylidene)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.26 mM of formate was obtained after 17 h reaction time.

xi. metal complex: [**Cu**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**);

40 mg of [**Cu**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.36 mM of formate was obtained after 18 h reaction time.

xii. metal complex: [**Cu**Cl(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)] (**E**); **Pws**: *m*tppts-Na_3

17 mg of previously prepared [CuCl(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)] and 19 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.3855 mM of formate was obtained in 25 h.

Example 15: Studies of nickel complex catalysts in hydrogenation.

i. metal salt: **Ni**CO_3; **NHC** precursor: 1-ethyl-3-methylimidazolium chloride; **Pws**: *m*tppts-Na_3

20 mg of $NiCO_3$ (0.168 mmol), 30 mg of 1-ethyl-3-methylimidazol-2-ylidene(HCl) (0.205 mmol) and 50 mg of *m*tppts-Na_3 (0.08 mmol) were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 40 bar H_2 pressure. By HPLC, 1 mM and 2.3 mM of formate were obtained after 2 h and 4 h reaction time, respectively.

ii. metal complex: [**Ni**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**);

10 mg of previously prepared [$NiCl_2$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (0.012 mmol) was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor,

and then 40 mg of K-hydrogencarbonate (0.4 mmol) was added. The hydrogenation was carried out at 80°C under 40 bar H_2 pressure. By HPLC, 0.1 mM and 0.2 mM of formate were obtained after 2 h and 4 h reaction time, respectively.

iii. metal complex: [**Ni**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] (**A**);

10 mg of [**Ni**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.28 mM of formate was obtained after 18 h reaction time.

iv. metal complex: [**Ni**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] (**A**); **Pws**: *m*tppts-Na_3

20 mg of [**Ni**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 6.06 mM of formate was obtained after 2 h reaction time.

v. metal complex: [**Ni**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] (**A**); **Pws**: *m*tppms-Na

40 mg of [**Ni**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] and 40 mg of *m*tppms-Na were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 1.18 mM of formate was obtained after 2 h reaction time.

vi. metal complex: [**Ni**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**); **Pws**: *m*tppts-Na_3

10 mg of [**Ni**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 H_2 pressure. By HPLC, 0.54 mM of formate was obtained after 4 h reaction time.

vii. metal complex: [**Ni**Cl_2(1-butyl-3-methylimidazol-2-ylidene)] (**A**); **Pws**: *m*tppts-Na_3

13 mg of [**Ni**Cl_2(1-butyl-3-methylimidazol-2-ylidene)] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.66 mM and 1.14 mM of formate were obtained after 2 h and 5 h reaction time, respectively.

viii. metal complex: [**Ni**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**);

10 mg of [**Ni**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and than 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.44 mM of formate was obtained after 20 h reaction time.

ix. metal complex: [**Ni**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**); **Pws**: *m*tppts-Na_3

20 mg of [**Ni**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and than 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.37 mM of formate was obtained after 4 h reaction time.

x. metal complex: [**Ni**Cl_2(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)] (**A**); **Pws**: *m*tppts-Na_3

7.5 mg of [$NiCl_2$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)] and 7.5 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. Hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.252 mM and 0.342 mM of formate were obtained after 4 h and 17 h reaction time, respectively.

xi. metal complex: [**Ni**Cl_2(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] (**A**);

20 mg of [$NiCl_2$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at

80°C under 30 bar H_2 pressure. By HPLC, 0.303 mM and 0.349 mM formate were obtained after 4 h and 17 h reaction time, respectively.

Example 16: Studies of manganese complex catalysts during hydrogenation.

i. metal complex: [**Mn**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**)

10 mg of previously prepared [$MnCl_2$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (0.012 mmol) was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 40 mg of K-hydrogencarbonate (0.4 mmol) was added. The hydrogenation was carried out at 80°C under 40 bar H_2 pressure. By HPLC, 0.1 mM and 0.2 mM of formate were obtained after 19 h and 4 h reaction time.

ii. metal complex: [**Mn**Cl_2(*m*tppts-Na_3)$_2$] (**A**);

15 mg of previously prepared [$MnCl_2$(*m*tppts-Na_3)$_2$] (0.016 mmol) was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 100 mg of K-hydrogencarbonate (1 mmol) was added. The hydrogenation was carried out at 80°C under 40 bar H_2 pressure. By HPLC, 0.9-1.0 mM of formate was obtained after 2 h reaction time.

iii. metal complex: [**Mn**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] (**A**); **Pws**: *m*tppts-Na_3

20 mg of [$MnCl_2$(1-ethyl-3-methylimidazol-2-ylidene)] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.45 mM of formate was obtained after 4 h reaction time.

iv. metal complex: [**Mn**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] (**A**); **Pws**: *m*tppts-Na_3

40 mg of [$MnCl_2$(1-ethyl-3-methylimidazol-2-ylidene)] and 40 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 2.08 mM of formate was obtained after 17 h reaction time.

v. metal complex: [**Mn**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] (**A**); **Pws**: *m*tppms-Na

20 mg of [$MnCl_2$(1-ethyl-3-methylimidazol-2-ylidene)] and 20 mg of *m*tppms-Na were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.24 mM of formate was obtained after 4 h reaction time.

vi. metal complex: [**Mn**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)] (**A**); **Pws**: *m*tppms-Na

40 mg of [$MnCl_2$(1-ethyl-3-methylimidazol-2-ylidene)] and 40 mg of *m*tppms-Na were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 1.19 mM and 3.72 mM of formate were obtained after 4 h and 66 h reaction time, respectively.

vii. metal complex: [**Mn**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**); **Pws**: *m*tppts-Na_3

20 mg of [$MnCl_2$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.31 mM of formate was obtained after 4 h reaction time.

viii. metal complex: [**Mn**Cl_2(1-butyl-3-methylimidazol-2-ylidene)] (**A**); **Pws**: *m*tppts-Na_3

20 mg of [$MnCl_2$(1-butyl-3-methylimidazol-2-ylidene)] and 20 mg of *m*tppts-Na_3 were weighed to 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.77 mM of formate was obtained after 4 h reaction time.

ix. metal complex: [**Mn**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**); **Pws**: *m*tppts-Na_3

20 mg of [$MnCl_2$(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] and 20 mg of *m*tppts-Na_3 were weighed to 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried

out at 80°C under 30 bar H_2 pressure. By HPLC, 0.32 mM of formate was obtained after 4 h reaction time.

x. metal complex: [**Mn**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**); **Pws**: *m*tppms-Na

20 mg of [$MnCl_2$(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] and 20 mg of *m*tppms-Na were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.54 mM of formate was obtained after 4 h reaction time.

xi. metal complex: [**Mn**Br$(CO)_4$(1-ethyl-3-methylimidazol-2-ylidene)] (**B**);

50 mg of [MnBr$(CO)_4$(1-ethyl-3-methylimidazol-2-ylidene)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 1.35 mM of formate was obtained after 17 h reaction time.

xii. metal complex: [**Mn**Br$(CO)_4$(1-ethyl-3-methylimidazol-2-ylidene)] (**B**); **Pws**: *m*tppts-Na_3

20 mg of [MnBr$(CO)_4$(1-ethyl-3-methylimidazol-2-ylidene)] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 2.61 mM of formate was obtained after 17 h reaction time.

xiii. metal complex: [**Mn**Br$(CO)_3$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**B**); **Pws**: *m*tppts-Na_3

20 mg of [MnBr$(CO)_3$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.57 mM of formate was obtained after 4 h reaction time.

xiv. metal complex: [**Mn**Br(CO)$_2$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)$_2$] (**B**); **Pws**: *m*tppts-Na$_3$

20 mg of [MnBr(CO)$_2$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)$_2$] and 20 mg of *m*tppts-Na$_3$ were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 1.78 mM of formate was obtained after 20 h reaction time.

xv. metal complex: [**Mn**Cl$_2$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na$_3$)] (**E**)

23 mg of previously prepared [MnCl$_2$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na$_3$)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 2.0316 mM of formate was obtained in 25 h.

xvi. metal complex:
[MnCl$_2$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppms-Na)] (**E**)

40 mg of previously prepared [MnCl$_2$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppms-Na)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 2.6511 mM of formate was obtained in 66 h.

Example 17: Studies of iron complex catalysts during hydrogenation.

i. metal complex: [**Fe**Cl$_2$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na$_3$)] (**A**)

10 mg of previously prepared [FeCl$_2$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na$_3$)] (0.012 mmol) was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 40 mg of K-hydrogencarbonate (0.4 mmol) was added. The hydrogenation was carried out at 80°C under 40 bar H_2 pressure. By HPLC, 0.8 and 1.2 mM of formate were obtained after 17 and 19 h reaction time, respectively.

ii. metal complex: [**Fe**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)$_2$] (**A**);

20 mg of [$FeCl_2$(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)$_2$] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 12.26 mM of formate was obtained after 4 h reaction time.

iii. metal complex: [**Fe**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)$_2$] (**A**); **Pws**: *m*tppts-Na_3

20 mg of [$FeCl_2$(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)$_2$] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 3.23 mM of formate was obtained after 17 h reaction time.

iv. metal complex: [**Fe**Cl_2(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)] (**E**); **Pws**: *m*tppts-Na_3

20 mg of [$FeCl_2$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)] and 20 mg of *m*tppts-Na_3 were weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 1.93 mM and 2.25 mM of formate was obtained after 3 h and 18 h reaction time, respectively.

v. metal complex: [**Fe**Cl_2(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] (**E**);

11 mg of [$FeCl_2$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.336 mM and 0.444 of mM formate were obtained after 3 h and 18 h reaction time, respectively.

Example 18: Studies of lanthanum complex catalysts in hydrogenation.

i. metal complex: [**La**Cl_3(1-butyl-3-methylimidazol-2-ylidene)] (**A**)

20 mg of previously prepared [$LaCl_3$(1-butyl-3-methylimidazol-2-ylidene)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.17 mM and 0.32 mM formate were obtained after 4 h and 18 h reaction time, respectively.

ii. metal complex: [**La**Cl_3(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**)

10 mg of previously prepared [$LaCl_3$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (0.013 mmol) was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.27 mM of formate was obtained after 42 h reaction time.

iii. metal complex: [**La**Cl_3(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**)

40 mg of previously prepared [$LaCl_3$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (0.04 mmol) was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.76 mM of formate was obtained after 42 h reaction time.

iv. metal complex: [**La**Cl_3(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**)

46 mg of previously prepared [$LaCl_3$(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.15 mM of formate was obtained after 17 h reaction time.

v. metal complex: [**La**Cl_3(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**)

20 mg of previously prepared [$LaCl_3$(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.09 mM of formate was obtained after 17 h reaction time.

vi. metal complex: [**La**Cl_3(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)] (**E**)
Pws: *m*tppts-Na_3

40 mg of [$LaCl_3$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)] and 40 mg of *m*tppts-Na_3 were weiged to 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2.0 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 2.3474 mM and 4.007 mM of formate were obtained after 3 h and 18 h reaction time, respectively.

Example 19: Studies of tin complex catalysts in hydrogenation.

i. metal complex: [**Sn**Cl_2(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**)

67 mg of previously prepared [$SnCl_2$(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.08 mM and 0.18 mM of formate were obtained after 4 h and 17 h reaction time, respectively.

ii. metal complex: [**Sn**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**)

40 mg of previously prepared [$SnCl_2$(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.336 mM of formate was obtained in 17 h.

iii. metal complex: [**Sn**Cl_2(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**)

40 mg of previously prepared [$SnCl_2$(1-butyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.154 mM and 0.249 mM of formate were obtained in 4 h and in 18 h, respectively.

iv. metal complex: [**Sn**Cl_2(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] (**E**)

40 mg of previously prepared [$SnCl_2$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.1178 mM of formate was obtained in 25 h.

Example 20: Studies of titanium complex catalysts in hydrogenation.

i. metal complex: [**Ti**OSO_4(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**)

10 mg of previously prepared [$TiOSO_4$(1-butyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.303 mM of formate was obtained in 17 h.

Example 21: Studies of vanadium complex catalysts in hydrogenation.

i. metal complex: [**V**O_3(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**)

47 mg of previously prepared [VO_3(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] was measured into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.9168 mM of formate was obtained in 4 h.

ii. metal complex: [**V**O_3(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] (**E**)

40 mg of previously prepared [VO_3(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 4.3917 mM of formate was obtained in 21 h.

Example 22: Studies of chromium complex catalysts during hydrogenation.

i. metal complex: [**Cr**Cl_3(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] (**E**)

26 mg of previously prepared [$CrCl_3$(1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.6509 mM and 1.3409 mM of formate was obtained in 3 h and in 18 h reaction time, respectively.

ii. metal complex: [**Cr**Cl_3(1-butyl-3-methylimidazol-2-ylidene)] (**A**)

40 mg of the previously prepared [$CrCl_3$(1-butyl-3-methylimidazol-2-ylidene)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 1.1661 mM of formate was obtained in 66 h.

Example 23: Studies of yttrium complex catalysts in hydrogenation.

i. metal complex: [**Y**Cl_3(1-ethyl-3-methylimidazol-2-ylidene)] (**A**)

43 mg of previously prepared [YCl_3(1-ethyl-3-methylimidazol-2-ylidene)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 1.2663 mM of formate was obtained in 21 h.

ii. metal complex: [**Y**Cl_3(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**)

40 mg of previously prepared [YCl_3(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.4548 mM of formate was obtained in 21 h.

iii. metal complex: [**Y**Cl_3(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**)

40 mg of previously prepared [YCl_3(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.3322 mM of formate was obtained in 21 h.

Example 24: Studies of molybdenum complex catalysts during hydrogenation.

i. metal complex: [**Mo**O_4(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] (**A**)

40 mg of previously prepared [MoO_4(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppms-Na)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.3165 mM of formate was obtained in 66 h.

ii. metal complex: [**Mo**O_4(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] (**A**)

40 mg of previously prepared [MoO_4(1-ethyl-3-methylimidazol-2-ylidene)(*m*tppts-Na_3)] was weighed into 20.0 mL of water pre-bubbled with N_2 in a 100 mL reactor, and then 200 mg of K-hydrogencarbonate (2 mmol) was added. The hydrogenation was carried out at 80°C under 30 bar H_2 pressure. By HPLC, 0.078 mM of formate was obtained in 66 h.

INDUSTRIAL APPLICABILITY

The catalyst and method described in this specification provide a means for the economically advantageous and cost-effective implementation of a hydrogen gas storage system and a hydrogen gas release system suitable for storing hydrogen gas produced from renewable resources, preferably by implementing the storage of hydrogen gas and the release of hydrogen gas in a single system (hydrogen accumulator) in the presence of the same catalyst. The hydrogen gas release system ensures the production of hydrogen gas free of CO_x by-products and enables the operation of the hydrogen gas storage system and the hydrogen gas release system without the continuous or cyclical addition of auxiliary materials (acids or bases).

Claims

1. Use of an isolated or non-isolated (*in situ* generated) catalyst comprising an **M** central metal and at least one strong sigma-donor ligand selected from the group consisting of **NHC** N-heterocyclic carbene ligands and **Pws** water-soluble phosphine ligands, in a process for storing hydrogen gas and/or in a process for releasing hydrogen gas, wherein the storage of hydrogen gas and the release of hydrogen gas are based on formate-bicarbonate equilibrium, wherein:

M is selected from non-platinum transition metals, p-field metals and f-field metals;

NHC is an N-heterocyclic carbene ligand, preferably selected from the group consisting of: 1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), 1-R^1-3-R^2-imidazol-2-ylidene, 1-R^1-3-R^2-imidazolin-2-ylidene and 1-R^1-3-R^2-benzimidazol-2-ylidene, wherein R^1 and R^2 are each independently a straight or branched chain alkyl group of 1 to 6 carbon atoms or a benzyl group, or a phenyl group, which is unsubstituted or substituted with an alkyl group of 1 to 6 carbon atoms;

Pws is a water soluble phosphine ligand selected from the group consisting of:

a tertiary phosphine of general formula $PR^1R^2R^3$ wherein R^1, R^2 and R^3 are independently a straight or branched chain alkyl group of 1 to 5 carbon atoms or a phenyl group, wherein the alkyl group may be substituted with an OH group or a sulphonato group and the phenyl group may be substituted with an alkyl group of 1 to 6 carbon atoms and/or a sulphonato group, provided that at least one of R^1, R^2 and R^3 carries an OH group or a sulphonato group; or

a cyclic tertiary phosphine; or

a diphosphine of general formula $R^4{}_2P$-*bridge*-$PR^5{}_2$, wherein R^4 and R^5 are independently a straight or branched chain alkyl group of 1 to 5 carbon atoms, or a phenyl group, wherein the alkyl group may be substituted with an OH group or a sulfonato group, and the phenyl group may be substituted with an alkyl group of 1 to 6 carbon atoms or a sulfonato group, wherein $PR^4{}_2$ and $PR^5{}_2$ may have the same or different meanings, provided that at least one of R^4 and R^5 carries an OH group or a sulphonato group; wherein the *bridge* group is a straight chain

alkylene group of 1 to 6 carbon atoms, preferably a methylene, ethylene, propylene, butylene or hexylene group; or

a diphosphine, which comprises cyclic tertiary phosphino groups linked by a covalent bonded bridge.

2. The use according to claim 1, wherein **M** in the catalyst is selected from the group consisting of non-platinum transition metals, lanthanum and tin.

3. The use according to claim 2, wherein **M** in the catalyst is selected from the group consisting of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, yttrium, molybdenum, lanthanum and tin.

4. The use according to claim 2, wherein **M** in the catalyst is selected from the group consisting of non-platinum transition metals.

5. The use according to claim 4, wherein **M** in the catalyst is selected from titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, yttrium and molybdenum.

6. The use according to any one of claims 1 to 5, wherein **NHC** in the catalyst is selected from the group consisting of: (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), 1,3-dimethylimidazol-2-ylidene, 1-ethyl-3-methylimidazol-2-ylidene (emim), 1-methyl-3-propylimidazol-2-ylidene, 1-butyl-3-methylimidazol-2-ylidene (bmim), 1-methyl-3-pentylimidazol-2-ylidene, 1,3-diethylimidazol-2-ylidene, 1-ethyl-3-propylimidazol-2-ylidene, 1-ethyl-3-butylimidazol-2-ylidene, 1-ethyl-3-pentylimidazol-2-ylidene, 1,3-dipropylimidazol-2-ylidene, 1-propyl-3-butylimidazol-2-ylidene, 1-propyl-3-pentylimidazol-2-ylidene, 1,3-dibutylimidazol-2-ylidene, 1-butyl-3-pentylimidazol-2-ylidene, 1,3-dipentylimidazol-2-ylidene; 1,3-diizopropylimidazol-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)imidazol-2-ylidene; 1-methyl-3-phenylimidazol-2-ylidene, 1-ethyl-3-phenylimidazol-2-ylidene, 1-propyl-3-phenylimidazol-2-ylidene, 1-butyl-3-phenylimidazol-2-ylidene, 1-pentyl-3-phenylimidazol-2-ylidene, 1,3-diphenylimidazol-2-ylidene; 1-benzyl-3-methylimidazol-2-ylidene (Bnmim), 1-hexyl-3-methylimidazol-2-ylidene (hexmim), 1,3-dimethylimidazolin-2-ylidene, 1-methyl-3-ethylimidazolin-2-ylidene, 1-methyl-3-propylimidazolin-2-ylidene, 1-methyl-3-butylimidazolin-2-ylidene, 1-methyl-3-pentylimidazolin-2-ylidene, 1,3-diethylimidazolin-2-ylidene, 1-ethyl-3-propylimidazolin-2-ylidene, 1-ethyl-3-butylimidazolin-2-ylidene, 1-ethyl-3-pentylimidazolin-2-ylidene, 1,3-

dipropylimidazolin-2-ylidene, 1-propyl-3-butylimidazolin-2-ylidene, 1-propyl-3-pentylimidazolin-2-ylidene, 1,3-dibutylimidazolin-2-ylidene, 1-butyl-3-pentylimidazolin-2-ylidene, 1,3-dipentylimidazolin-2-ylidene; 1,3-diizopropylimidazolin-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)imidazolin-2-ylidene; 1-methyl-3-phenylimidazolin-2-ylidene, 1-ethyl-3-phenylimidazolin-2-ylidene, 1-propyl-3-phenylimidazolin-2-ylidene, 1-butyl-3-phenylimidazolin-2-ylidene, 1-pentyl-3-phenylimidazolin-2-ylidene, 1,3-diphenylimidazolin-2-ylidene; 1,3-dimethylbenzimidazol-2-ylidene, 1-methyl-3-ethylbenzimidazol-2-ylidene, 1-methyl-3-propylbenzimidazol-2-ylidene, 1-methyl-3-butylbenzimidazol-2-ylidene, 1-methyl-3-pentylbenzimidazol-2-ylidene, 1,3-diethylbenzimidazol-2-ylidene, 1-ethyl-3-propylbenzimidazol-2-ylidene, 1-ethyl-3-butylbenzimidazol-2-ylidene, 1-ethyl-3-pentylbenzimidazol-2-ylidene, 1,3-dipropylbenzimidazol-2-ylidene, 1-propyl-3-butylbenzimidazol-2-ylidene, 1-propyl-3-pentylbenzimidazol-2-ylidene, 1,3-dibutylbenzimidazol-2-ylidene, 1-butyl-3-pentylbenzimidazol-2-ylidene, 1,3-dipentylbenzimidazol-2-ylidene; 1,3-diizopropylbenzimidazol-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)benzimidazol-2-ylidene; 1-methyl-3-phenylbenzimidazol-2-ylidene, 1-ethyl-3-phenylbenzimidazol-2-ylidene, 1-propyl-3-phenylbenzimidazol-2-ylidene, 1-butyl-3-phenylbenzimidazol-2-ylidene, 1-pentyl-3-phenylbenzimidazol-2-ylidene and 1,3-diphenylbenzimidazol-2-ylidene.

7. The use according to any one of claims 1 to 6, wherein **Pws** in the catalyst is selected from the group consisting of:

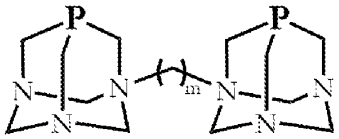
a tertiary phosphine of general formula $PR^1R^2R^3$ selected from the group consisting of: $P(CH_2OH)_3$ [tris(hydroxymethyl)phosphine], Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *ortho* position (*o*tppms, *o*tppds, *o*tppts); Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts); or Li, Na, K or Cs salt of a triphenylphosphine, which is monosulfonated in the *para* position (*p*tppms); and

1,3,5-triaza-7-phosphaadamantane (pta).

8. The use according to any one of claims 1 to 6, wherein **Pws** in the catalyst is selected from the group consisting of:

a phosphine of general formula R^4_2P-*bridge*-PR^5_2 wherein PR^4_2 and PR^5_2 are independently selected from: $P(CH_2OH)_2$ (bis(hydroxymethyl)phosphino group), PPh_2 (diphenylphosphino group), Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *ortho* position; Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *meta* position; Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *para* position, *'bridge'* represents an alkylene group of 1 to 6 carbon atoms; and

compounds according to formula (4):



formula (4)

where m in formula (4) is an integer from 1 to 6.

9. The use according to claim 7, wherein **Pws** in the catalyst is selected from the group consisting of Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts); 1,3,5-triaza-7-phosphaadamantane (pta).

10. The use according to claim 8, wherein **Pws** in the catalyst is selected from the group consisting of tetrasulfonated 1,2-bis(diphenylphosphino)ethane (dppets), tetrasulfonated 1,3-bis(diphenylphosphino)propane (dpppts), and the compound of formula (4).

11. The use according to any one of claims 1 to 10, wherein **NHC** in the catalyst is selected from the group consisting of: 1-ethyl-3-methylimidazol-2-ylidene (emim); 1-butyl-3-methylimidazol-2-ylidene (bmim); 1-hexyl-3-methylimidazol-2-ylidene (hexmim) and 1-benzyl-3-methylimidazol-2-ylidene (Bnmim); and (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron).

12. The use according to any one of claims 1 to 11, wherein the catalyst is represented by general formula (I), (II) or (III):

$$\mathbf{[M(NHC)_n(Pws)_p(L^1)_q(L^2)_r]}\ \text{(I), or}$$

$[Fe_3(NHC)_{n'}(Pws)_{p'}(L^1)_{q'}(L^2)_{r'}]$ (II), or

$[Co_2(NHC)_{n''}(Pws)_{p''}(L^1)_{q''}(L^2)_{r''}]$ (III),

wherein

M, NHC and **Pws** are as defined in any of claims 1 to 11;

L^1 is a negatively charged ligand, preferably selected from the group consisting of: H^-, F^-, Cl^-, Br^-, I^-, OH^-, BF_4^-, PF_6^-, HCO_3^- (hydrogencarbonate), HCO_2^- (formate), $CH_3CO_2^-$ (acetate), $[CH_3COCHCOCH_3]^-$ (acetylacetonate), cyanide, isocyanide, nitrite, nitrate, thiocyanate, and isothiocyanate; SO_4^{2-} and O^{2-};

L^2 is a neutral (non-ionic) ligand selected from the group consisting of: H_2O, CO (carbonyl); MeOH; dimethylsulfoxide or acetonitrile; a cycloalkadiene of 5 to 10 ring members, optionally substituted with one or more substituents selected from alkyl groups of 1 to 5 carbon atoms and phenyl groups; a π-donor aromatic hydrocarbon ligand of 6 to 10 carbon atoms; and

in general formula (I), n, p, q and r are 0, 1, 2, 3 or 4, provided that n + p is at least 1 and $n + p + q + r \leq 8$;

in general formula (II), n' is 0 or 1, p' is 1, 2 or 3, q' is 0, r' = 12-n'-q'-r'-p';

in general formula (III), n" is 0 or 1, p" is 1 or 2, q" is 0, r" = 8-n"-q"-r"-p";

wherein, if n, p, q, r, n', p', q', r', n", p", q" and/or r" are greater than 1, then **NHC**, **Pws**, L^1 and/or L^2 may be the same or different.

13. The use according to claim 12, wherein

L^1 is H^-, F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$ (acetate), SO_4^{2-}, or O^{2-}; and

L^2 is CO, H_2O, MeOH or CH_3CN or dimethyl sulfoxide.

14. The use according to any one of claims 1 to 5, wherein the catalyst is represented by general formula (I), (II) or (III):

$[M(NHC)_n(Pws)_p(L^1)_q(L^2)_r]$ (I), or

$[Fe_3(NHC)_{n'}(Pws)_{p'}(L^1)_{q'}(L^2)_{r'}]$ (II), or

$[Co_2(NHC)_{n''}(Pws)_{p''}(L^1)_{q''}(L^2)_{r''}]$ (III),

wherein

NHC is selected from the group consisting of: (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), 1,3-dimethylimidazol-2-ylidene, 1-ethyl-3-methylimidazol-2-ylidene (emim), 1-methyl-3-propylimidazol-2-ylidene, 1-butyl-3-methylimidazol-2-ylidene (bmim), 1-methyl-3-pentylimidazol-2-ylidene, 1,3-diethylimidazol-2-ylidene, 1-ethyl-3-propylimidazol-2-ylidene, 1-ethyl-3-butylimidazol-2-ylidene, 1-ethyl-3-pentylimidazol-2-ylidene, 1,3-dipropylimidazol-2-ylidene, 1-propyl-3-butylimidazol-2-ylidene, 1-propyl-3-pentylimidazol-2-ylidene, 1,3-dibutylimidazol-2-ylidene, 1-butyl-3-pentylimidazol-2-ylidene, 1,3-dipentylimidazol-2-ylidene; 1,3-diizopropylimidazol-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)imidazol-2-ylidene; 1-methyl-3-phenylimidazol-2-ylidene, 1-ethyl-3-phenylimidazol-2-ylidene, 1-propyl-3-phenylimidazol-2-ylidene, 1-butyl-3-phenylimidazol-2-ylidene, 1-pentyl-3-phenylimidazol-2-ylidene, 1,3-diphenylimidazol-2-ylidene; 1-benzyl-3-methylimidazol-2-ylidene (Bnmim), 1-hexyl-3-methylimidazol-2-ylidene (hexmim), 1,3-dimethylimidazolin-2-ylidene, 1-methyl-3-ethylimidazolin-2-ylidene, 1-methyl-3-propylimidazolin-2-ylidene, 1-methyl-3-butylimidazolin-2-ylidene, 1-methyl-3-pentylimidazolin-2-ylidene, 1,3-diethylimidazolin-2-ylidene, 1-ethyl-3-propylimidazolin-2-ylidene, 1-ethyl-3-butylimidazolin-2-ylidene, 1-ethyl-3-pentylimidazolin-2-ylidene, 1,3-dipropylimidazolin-2-ylidene, 1-propyl-3-butylimidazolin-2-ylidene, 1-propyl-3-pentylimidazolin-2-ylidene, 1,3-dibutylimidazolin-2-ylidene, 1-butyl-3-pentylimidazolin-2-ylidene, 1,3-dipentylimidazolin-2-ylidene; 1,3-diizopropylimidazolin-2-ylidene; 1,3-di(2,4,6-trimethylphenyl)imidazolin-2-ylidene; 1-methyl-3-phenylimidazolin-2-ylidene, 1-ethyl-3-phenylimidazolin-2-ylidene, 1-propyl-3-phenylimidazolin-2-ylidene, 1-butyl-3-phenylimidazolin-2-ylidene, 1-pentyl-3-phenylimidazolin-2-ylidene, 1,3-diphenylimidazolin-2-ylidene; 1,3-dimethylbenzimidazol-2-ylidene, 1-methyl-3-ethylbenzimidazol-2-ylidene, 1-methyl-3-propylbenzimidazol-2-ylidene, 1-methyl-3-butylbenzimidazol-2-ylidene, 1-methyl-3-pentylbenzimidazol-2-ylidene, 1,3-diethylbenzimidazol-2-ylidene, 1-ethyl-3-propylbenzimidazol-2-ylidene, 1-ethyl-3-butylbenzimidazol-2-ylidene, 1-ethyl-3-pentylbenzimidazol-2-ylidene, 1,3-dipropylbenzimidazol-2-ylidene, 1-propyl-3-butylbenzimidazol-2-ylidene, 1-propyl-3-pentylbenzimidazol-2-ylidene, 1,3-

dibutylbenzimidazol-2-ylidene, 1-butyl-3-pentylbenzimidazol-2-ylidene, 1,3-dipentylbenzimidazol-2-ylidene; 1,3-diizopropylbenzimidazol-2-ylidene; 1,3-di(2,4,6-trimethylpheny)lbenzimidazol-2-ylidene; 1-methyl-3-phenylbenzimidazol-2-ylidene, 1-ethyl-3-phenylbenzimidazol-2-ylidene, 1-propyl-3-phenylbenzimidazol-2-ylidene, 1-butyl-3-phenylbenzimidazol-2-ylidene, 1-pentyl-3-phenylbenzimidazol-2-ylidene and 1,3-diphenylbenzimidazol-2-ylidene;

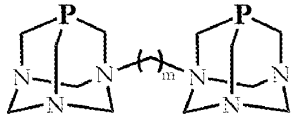
Pws is selected from the group consisting of:

a tertiary phosphine of general formula $PR^1R^2R^3$ selected from the group consisting of: $P(CH_2OH)_3$ [tris(hydroxymethyl)phosphine], Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *ortho* position (*o*tppms, *o*tppds, *o*tppts); Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts); and Li, Na, K or Cs salt of a triphenylphosphine, which is monosulfonated in the *para* position (*p*tppms);

1,3,5-triaza-7-phosphaadamantane (pta);

a phosphine of general formula $R^4{}_2P$-*bridge*-$PR^5{}_2$ wherein $PR^4{}_2$ and $PR^5{}_2$ are independently selected from: $P(CH_2OH)_2$ (bis(hydroxymethyl)phosphino group), PPh_2 (diphenylphosphino group), Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *ortho* position; Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *meta* position; Li, Na, K or Cs salt of a diphenylphosphino group, which is mono- or disulfonated in the *para* position; and

a compound of formula (4):



(4),

where m is an integer from 1 to 6;

L^1 is selected from the group consisting of: H^-, F^- Cl^-, Br^-, I^-, OH^-, BF_4^-, PF_6^-, HCO_3^- (hydrogencarbonate), HCO_2^- (formate), $CH_3CO_2^-$ (acetate), $[CH_3COCHCOCH_3]^-$ (acetylacetonate), cyanide, isocyanide, nitrite, nitrate, thiocyanate, and isothiocyanate, SO_4^{2-} and O^{2-};

L² is CO, H_2O, MeOH, CH_3CN or dimethyl sulfoxide;

in the general formula (I), n, p, q and r are 0, 1, 2, 3 or 4, provided that n + p is at least 1 and n + p + q + r ≤ 8;

in general formula (II), n' is 0 or 1, p' is 1, 2 or 3, q' is 0, r' = 12-n'-q'-r'-p';

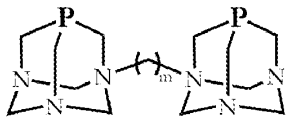
in general formula (III), n" is 0 or 1, p" is 1 or 2, q" is 0, r" = 8-n"-q"-r"-p";

where if n, p, q, r, n', p', q', r', n", p", q" and/or r" are greater than 1, then **NHC**, **Pws**, **L¹** and/or **L²** may be the same or different.

15. The use according to claim 14, wherein in general formula (I), (II) or (III)

NHC is 1-ethyl-3-methylimidazol-2-ylidene (emim), 1-butyl-3-methylimidazol-2-ylidene (bmim); 1-hexyl-3-methylimidazol-2-ylidene (hexmim), 1-benzyl-3-methylimidazol-2-ylidene (Bnmim), or 1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron);

Pws is a Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts), or 1,3,5-triaza-7-phosphadamantane (pta), tetrasulfonated 1,2-bis(diphenylphosphino)ethane (dppets), tetrasulfonated 1,3-bis(diphenylphosphino)propane (dpppts) or a compound of formula (4) below:



(4),

where m is an integer from 1 to 6,

L¹ is H^-, F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$ (acetate), SO_4^{2-} or O^{2-}; and

L² is CO, H_2O, MeOH, CH_3CN or dimethyl sulfoxide.

16. The use according to claim 15, wherein, in the catalyst of general formula (I), (II) or (III)

NHC is 1-ethyl-3-methylimidazol-2-ylidene (emim), 1-butyl-3-methylimidazol-2-ylidene (bmim); 1-hexyl-3-methylimidazol-2-ylidene (hexmim), 1-benzyl-3-methylimidazol-2-ylidene (Bnmim), or 1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron);

Pws is a Li, Na, K or Cs salt of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppts), or 1,3,5-triaza-7-phosphaadamantane (pta);

L^{1} is Cl^{-}, Br^{-}, $CH_3CO_2^{-}$, SO_4^{2-} or O^{2-}; and

L^{2} is CO or H_2O.

17. The use according to any one of claims 14 to 16, wherein, in the catalyst of general formula (I) n and p is 0, 1 or 2; q is 0, 1, 2, 3 or 4; and r is 0, 1, 2, 3 or 4, with the proviso that $n + p$ is at least 1 and $n + p + q + r \leq 8$.

18. The use according to any one of claims 1 to 5, wherein the catalyst is a catalyst generated *in situ* from the use of

a water-soluble salt of a metal **M** and at least 1 equimolar amount of an **NHC** precursor and/or **Pws** ligand with respect to the metal ion,

wherein

M, and **Pws** are as defined in any of claims 1 to 5;

NHC precursor is a precursor compound of an N-heterocyclic carbene, preferably selected from the group consisting of: (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron), and salts of 1-R^1-3-R^2-imidazolium, 1-R^1-3-R^2-imidazolinium and 1-R^1-3-R^2-benzimidazolium, wherein R^1 and R^2 are each independently a straight or branched chain alkyl group of 1 to 6 carbon atoms or a benzyl group, or a phenyl group, which is unsubstituted or substituted with an alkyl group of 1 to 6 carbon atoms.

19. The use according to claim 18, wherein, for the generation of the non-isolated catalyst, the used

NHC precursor is selected from: 1-ethyl-3-methylimidazolium chloride (emimCl); 1-butyl-3-methylimidazolium chloride (bmimCl); 1-hexyl-3-methylimidazolium chloride

(hexmimCl), 1-benzyl-3-methylimidazolium chloride (BnmimCl); 1-ethyl-3-methylimidazolium acetate (emimAc); 1-butyl-3-methylimidazolium acetate (bmimAc); 1-hexyl-3-methylimidazolium acetate (hexmimAc) and 1-benzyl-3-methylimidazolium acetate (BnmimAc); and (1,4-diphenyl-1*H*-1,2,4-triazol-4-ium-3-yl)(phenyl)azanide (nitron);

Pws is selected from: Li, Na, K or Cs salts of a triphenylphosphine, which is mono-, di- or trisulfonated in the *meta* position (*m*tppms, *m*tppds, *m*tppts), or 1,3,5-triaza-7-phosphadamantane (pta).

20. The use according to claim 18 or 19, wherein the at least 1 equimolar amount of **NHC** precursor and/or **Pws** ligand with respect to metal ion **M**, used to form the non-isolated catalyst, is 0-10 equimolar amount of **NHC** precursor and 0-10 equimolar amount **Pws** ligand, preferably 0-6 equimolar amount of **NHC** precursor and 0-6 equimolar amount **Pws** ligand, more preferably 1-6 equimolar amount of **NHC** precursor and/or **Pws** ligand, with respect to the metal ion **M**.

21. Process for releasing hydrogen gas, wherein the process comprises the decomposition of formate, preferably sodium formate (HCO_2Na), lithium formate (HCO_2Li), cesium formate (HCO_2Cs) and/or potassium formate (HCO_2K) in an aqueous reaction system in the presence of a catalyst as defined in any of claims 1 to 20, to produce hydrogen gas free of CO_x by-products,

wherein the decomposition of the formate is carried out in an oxygen-free atmosphere at elevated temperature, preferably at 60-100°C, more preferably at 60-80°C, at a pH greater than 8, preferably at pH=8.3±0.2.

22. Process for storing hydrogen gas, wherein the process comprises hydrogenating hydrogencarbonate (HCO_3^-), preferably sodium hydrogencarbonate ($NaHCO_3$), lithium hydrogencarbonate ($LiHCO_3$), cesium hydrogencarbonate ($CsHCO_3$) and/or potassium hydrogencarbonate ($KHCO_3$) in an aqueous reaction system in the presence of a catalyst as defined in any one of Claims 1 to 20, to produce a formate, preferably sodium formate (HCO_2Na), lithium formate (HCO_2Li), cesium formate (HCO_2Cs) and/or potassium formate (HCO_2K),

wherein the step of hydrogenation of hydrogencarbonate is carried out in an oxygen-free atmosphere at elevated temperature, preferably at 60-100°C, more preferably at 80°C, at a

H_2 pressure of 1-1200 bar, preferably 10-100 bar, more preferably 30-40 bar, more preferably 30 or 40 bar.

23. Process for releasing hydrogen gas and storing hydrogen gas, wherein the process comprises the steps of:

i) decomposition of formate, preferably sodium formate (HCO_2Na), lithium formate (HCO_2Li), cesium formate (HCO_2Cs) and/or potassium formate (HCO_2K) in an aqueous reaction system in the presence of a catalyst as defined in any one of claims 1 to 20, to produce hydrogen gas (H_2) free of CO_x by-products; and

ii) hydrogenation of the hydrogencarbonate (HCO_3^-), preferably sodium hydrogencarbonate ($NaHCO_3$), lithium hydrogencarbonate ($LiHCO_3$), cesium hydrogencarbonate ($CsHCO_3$) and potassium hydrogencarbonate ($KHCO_3$), produced in step i) in an aqueous reaction system in the presence of the catalyst used in step i), to produce formate, preferably sodium formate (HCO_2Na), lithium formate (HCO_2Li), cesium formate (HCO_2Cs) and/or potassium formate (HCO_2K);

wherein the decomposition of the formate is carried out in an oxygen-free atmosphere at elevated temperature, preferably at 60-100°C, more preferably at 60-80°C, at a pH greater than 8, preferably at pH=8.3±0.2;

and wherein the step of hydrogenation of hydrogencarbonate is carried out in an oxygen-free atmosphere at elevated temperature, preferably at 60-100°C, more preferably at 80°C, at a H_2 pressure of 1-1200 bar, preferably 10-100 bar, more preferably 30-40 bar, more preferably 30 or 40 bar;

and wherein the reactants and reaction products are formed in a reversible reaction cycle using the reaction system of the formate decomposition step and the hydrogencarbonate hydrogenation step, and optionally this reaction cycle is repeated.

24. Use of a process according to any one of claims 21 to 23 for a hydrogen storage system, preferably for a hydrogen accumulator.