

Water-Soluble Iridium-NHC-Phosphine Complexes as Catalysts for Chemical Hydrogen Batteries Based on Formate

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Molecular hydrogen, obtained by water electrolysis or photocatalytic water splitting, can be used to store energy obtained from intermittent sources such as wind and solar power. The storage and safe transportation of H_2 , however, is an open and central question in such a hydrogen economy. Easy-to-synthesize, water-soluble iridium-*N*-heterocyclic carbene-phosphine (Ir^I -NHC-phosphine) catalysts show unprecedented high catalytic activity in dehydrogenation of aqueous sodium formate. Fast reversible generation and storage of hydrogen can be achieved with these catalysts by a simple decrease or increase in the hydrogen pressure, respectively.

The boundless accumulation of carbon dioxide in the atmosphere is caused in a large part by burning fossil fuels. Fossil fuels can be replaced by renewable energy, however, new methodologies have to be developed to make the latter suitable for use in everyday life, and one possibility is its storage in the form of easy-to-handle chemicals. Hydrogen has long been suggested as such a chemical because its reaction with oxygen in fuel cells provides electric energy for universal use (i.e., the hydrogen economy). Owing to natural fluctuations in the supply of solar, wind, and other forms of renewable energy, H₂ (obtained by water electrolysis or photocatalytic water splitting) can be useful as an energy storage material provided there are suitable physical or chemical systems in which the hydrogen itself can be stored and from which it can be liberated at will.

Formic acid is one of the most promising compounds for hydrogen storage. Several efficient homogeneous^[1] and heterogeneous^[2] catalysts have been developed for decomposition of HCO_2H ; the reaction supplies hydrogen that can be used in fuel cells. However, decomposition of formic acid also yields CO_2 , in addition to H_2 . Although direct hydrogenation of CO_2 to formic acid (required to construct a closed hydrogen storage/delivery cycle) has been demonstrated,^[3] practical hydro-

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	Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201500808

genation of CO₂ is feasible only in the presence of inorganic or organic bases, for example various amines.^[4] In other cases, the activity of the often exceedingly active^[5c] pH-responsive Ir¹-based catalysts has to be switched between hydrogenation of HCO₃⁻ and dehydrogenation of HCO₂⁻ (in fact: HCO₂H) by setting the optimum pH for the given reaction with external acid and base in each cycle.^[5]

As a possible answer to these problems, we developed the first purely inorganic reaction system^[6] in which the formatebicarbonate charge-discharge cycles (Scheme 1) are catalyzed

$$HCO_3^{-} + H_2 \implies HCO_2^{-} + H_2C$$

Scheme 1. Storage and release of H₂ in the bicarbonate/formate equilibrium.

by the same Ru^{II}-complex, [{RuCl₂(*m*tppms-Na)₂]₂] (*m*tppms-Na = monosulfonated triphenylphosphine sodium salt). Dehydrogenation of formate in this aqueous reaction mixture yielded CO-free H₂ together with bicarbonate. As a result, storage and delivery of H₂ could be alternated simply by changing the pressure of H₂ with no need of any additives. Very recently a similar system was described, with inorganic formate salts as storage material and Ru^{II}-PNP pincer complexes as catalysts in water–THF or water–dioxane mixtures.^[7]

During our research into the synthesis and catalytic application of water-soluble iridium(I)-N-heterocyclic carbene-phosphine complexes in hydrogenation and in redox isomerization in aqueous solutions,^[8a] we noticed that the same complexes also catalyzed the decomposition of aqueous sodium formate to yield CO-free gaseous H2.[8b] Therefore, the most active catalysts, that is, [lr(cod)(emim)(*m*tppms)] (1) and $Na_2[Ir(cod)(emim)(mtppts)]$ (2) (cod = 1,5-octadiene, emim = 1ethyl-3-methylimidazol-2-ylidene, mtppts-Na₃ = trisulfonated triphenylphosphine sodium salt; Scheme 2), were studied in detail both in formate dehydrogenation and in bicarbonate hydrogenation. These catalysts, as well as $Na_2[Ir(bmim)(cod)(mtppts)]$ (3) (bmim = 1-butyl-3-methylimida-



Scheme 2. Water-soluble iridium-N-heterocyclic carbene-phosphine catalysts.

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Figure 1. Time course of hydrogen evolution from aqueous HCO_2Na solutions catalyzed by $Na_2[lr(cod)(emim)(mtppts)]$ (2) + 2 *m*tppts at various $[HCO_2^{-}]/[lr]$ ratios: \bullet 3000; \bullet 4200; \bullet 5000; \bullet 7500; \bullet 10000. [2] = 0.5 mm; *m*tppts = 1.0 mm; *V*(H₂O) = 10 mL; *T* = 80 °C, *P*(total) = 1 bar.

zol-2-ylidene) can also be obtained in situ in the reaction of [IrCl(cod)(NHC)] and *m*tppms-Na or *m*tppts-Na₃ (NHC = emim or bmim).^[8a]

Figure 1 shows the rapid evolution of H₂ from aqueous HCO₂Na solutions on catalysis by 2+2 *m*tppts (the highest initial TOF of H₂ evolution was 11240 h⁻¹; Supporting Information, Table S1). Note that the catalyst tolerates very high substrate/catalyst ratios (\geq 10000)—this is important for constructing hydrogen batteries of high capacity. In general, **1** is more active than **2** (Table S1), however, it has lower solubility and does not dissolve completely in \geq 2.1 \times HCO₂Na solutions. However, in the presence of 2 equiv *m*tppts the solutions of **1** remained homogeneous even at 5 \times HCO₂Na concentration and yielded H₂ with an unprecedented high turnover frequency (TOF) of 15 110 h⁻¹ at 80 °C.

Dehydrogenation of formate in a closed system results in increased H_2 pressure. Hydrogen evolution stops when thermodynamic conditions of the bicarbonate–formate equilibrium (Scheme 1) are reached. Under our conditions, in the first cycle the equilibrium pressure was 5.9 bar, corresponding to 0.4 L of H_2 from 10 mL aqueous solution. When releasing the pressure, hydrogen generation resumed and reached a new equilibrium at a lower pressure (owing to decreased formate concentration) (Figure 2).

Discharge-charge cycles of a hydrogen battery were modelled in a 5 mm high-pressure NMR tube using $H^{13}CO_2Na$.

Figure 3 shows that in the discharge step HCO2-/H2O was decomposed to H_2 and HCO_3^- in about 30 min. Increasing the H₂ pressure to 100 bar resulted in a fast hydrogenation of HCO3- HCO_{2}^{-} (charging; TOF >to 310 h⁻¹; see also Supporting Information, Table S2). Upon release of the pressure, dehydrogenation of formate took place again. The catalyst retained its full activity even after storing the reaction mixture under 100 bar H₂ for 71 days at room temperature—as shown by four



Figure 2. Changes in the H₂ pressure (above atmospheric) upon catalytic formate dehydrogenation in a closed reactor. [1]=2 mm; [mtppms]=4 mm; [HCO₂Na]=2400 mm; V(H₂O)=10 mL; T=80 °C. At t=100 min and 220 min P(H₂) was set to atmospheric.



Figure 3. Reversible hydrogen storage in a formate-bicarbonate system. [Ir] = 10 mM, [mtppts] = 20 mM; [Ru] = 10 mM, [mtppms] = 42.5 mM; $[H^{13}CO_2Na] = 257 \text{ mM}; V(H_2O) = 0.5 \text{ mL}; T = 80 \degree C.$

new cycles on Figure S3 (Supporting Information). One cycle of hydrogen storage from our prior work^[6] with [{RuCl₂(mtppms-Na)₂}₂] catalyst is also shown in Figure 3.

The activities of various catalysts applied so far for hydrogen storage in aqueous formate systems are shown in Table 1. It is seen that the activity of [Ir(cod)(emim)(mtppms)] + mtppts is superior to that of all other catalysts. Because of this high activity, one discharge–charge cycle is completed in ≤ 60 min (Figure 3) while a similar discharge–charge cycle with the Ru^{II}-pincer complexes^[7] required 4 h *in each direction*. Note that other Ir-based catalysts are not listed in Table 1; in fact, the

Table 1. Activities of various catalysts of formate dehydrogenation.								
Catalyst	Solvent	M in HCO₂M	<i>Т</i> [°С]	$iTOF$ $[h^{-1}]^{[a,b]}$	Ref.			
Pd/C nanocat.	H ₂ O	Na	30	24.4	[9]			
Pd nanocat.	H ₂ O	NH_4	20	1800	[10]			
Pd/rGO ^[c]	H ₂ O	К	80	11 299	[11]			
$[{RuCl_2(benzene)}_2] + dppm^{[d]}$	DMF/H ₂ O	Li	60	2923	[12]			
$[{RuCl_2(benzene)}_2] + dppm$	DMF/H ₂ O	Na	60	2592	[12]			
Ru ^{II} -PNP pincers	dioxane/H ₂ O	Na	84	820	[7]			
$[{RuCl_2(mtppms-Na)_2}_2] + mtppms$	H ₂ O	Na	80	2600	[6]			
$[{RuCl_2(mtppts-Na_3)_2}_2] + mtppts$	H ₂ O	Na	80	19	[13]			
$[{RuCl_2(mtppts-Na_3)_2}_2] + mtppts$	H ₂ O	Cs	80	196	[13]			
[lr(cod)(emim)(<i>m</i> tppms)] + <i>m</i> tppts	H ₂ O	Na	80	15 110	this work			
[a] Initial TOF. [b] iTOF values taken from the literature or calculated from published data for reaction times ≤ 1 h. [c] rGO=reduced graphite oxide. [d] dppm= <i>bis</i> (diphenylphosphino)methane.								

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[IrH₃(PNP)] pincer complex (TOF = 120000 h⁻¹ in dehydrogenation of HCO₂(HNEt₃) in tBuOH) was completely inactive for dehydrogenation of HCO₂Na in water.^[14]

In conclusion, we demonstrate that the water-soluble Ir^I-NHC-phosphine type complexes have exceedingly high activity in dehydrogenation of aqueous sodium formate. This is the first time such complexes are used to catalyze these two reactions. The same complexes are also remarkably active in the hydrogenation of bicarbonate to formate. These features allow construction of additive-free, purely aqueous reversible hydrogen storage systems in which the fast charge–discharge processes are regulated solely by the hydrogen pressure.

Experimental Section

Experimental details can be found in the Supporting Information.

Acknowledgements

This research was supported by the EU and co-financed by the European Social Fund under the project ENVIKUT (TÁMOP-4.2.2A-11/1/KONV-2012-0043). We thanks the Hungarian Research Fund (OTKA K101372) for financial support. G.P. is grateful for a János Bolyai Research Scholarship of the Hungarian Academy of Sciences and for an internal research grant from the University of Debrecen.

Keywords: carbenes · homogeneous catalysis · hydrogen · iridium · phosphorus

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Received: June 15, 2015 Revised: July 14, 2015 Published online on August 19, 2015