

Reversible hydrogen storage using CO₂ and a proton-switchable iridium catalyst in aqueous media under mild temperatures and pressures

Jonathan F. Hull¹*, Yuichiro Himeda²*, Wan-Hui Wang², Brian Hashiguchi³, Roy Periana³, David J. Szalda⁴, James T. Muckerman¹ and Etsuko Fujita¹*

Green plants convert CO₂ to sugar for energy storage via photosynthesis. We report a novel catalyst that uses CO₂ and hydrogen to store energy in formic acid. Using a homogeneous iridium catalyst with a proton-responsive ligand, we show the first reversible and recyclable hydrogen storage system that operates under mild conditions using CO₂, formate and formic acid. This system is energy-efficient and green because it operates near ambient conditions, uses water as a solvent, produces high-pressure CO-free hydrogen, and uses pH to control hydrogen production or consumption. The extraordinary and switchable catalytic activity is attributed to the multifunctional ligand, which acts as a proton-relay and strong π -donor, and is rationalized by theoretical and experimental studies.

The efficient and catalytic reduction of CO₂ by photosynthesis has inspired many sustainable energy and ‘clean tech’ applications^{1–8}, because CO₂ is cheap, abundant and stable. CO₂ is also a greenhouse gas, and its fixation as part of a carbon-neutral energy cycle would significantly decrease its associated environmental risks⁹. Dihydrogen (H₂) is desirable as a fuel, because it can be converted efficiently to energy without producing toxic products or greenhouse gases, and the rates and efficiencies with which it can be obtained from water with sunlight continue to increase^{10,11}. However, on an industrial scale, H₂ is constrained by its physical properties, leading to safety concerns, transport problems and a low energy density⁴. Conventional research on H₂ storage devices such as high-pressure and cryogenic gas containers is unlikely to overcome these problems, and the results have not proved economically viable¹². Other approaches using new materials such as metal hydrides and metal organic frameworks have also been investigated, but these are limited by their high activation energy and low energy density¹³. In contrast, liquids with a high (>4%) hydrogen content can be safe to handle, offer greater energy density, and can be transported easily using the existing infrastructure for gasoline and oil. Aqueous formic acid (HCO₂H) and its conjugate base, formate (HCO₂[–]), are promising liquid hydrogen-storage media because of the low energy barrier to their formation from H₂ and CO₂ ($\Delta G^\circ_{298} = -4 \text{ kJ mol}^{-1}$)^{5,14–19}. The equilibrium, given by



may therefore be viewed as a hydrogen storage system, with fuel-ready H₂ on the left-hand side, and stored H₂ on the right. Although formic acid fuel cells²⁰ and industrial processes that consume formic acid could be made more cost-effective by using reduced CO₂ as a C1 feedstock, we focus only on hydrogen storage in this study.

There has been excellent recent progress in developing catalysts targeted to either the reductive or oxidative components of hydrogen

storage using formic acid, that is, in the separate steps for the hydrogenation of CO₂ and the decomposition of HCO₂H, respectively^{15,21–43}. CO₂ hydrogenation has been achieved by Nozaki and colleagues using iridium pincer compounds, achieving rates as high as 150,000 h^{–1} at 200 °C and a turnover number (TON) of 3,500,000 at 120 °C (ref. 30). Langer and colleagues reported an iron pincer catalyst that operates at 156 h^{–1} and has a TON of 788 at 1 MPa and 80 °C (ref. 28). Meanwhile, Peris and colleagues have used alcohols in place of H₂ to obtain formate from CO₂ (refs 44–46). The high-pressure reduction of bicarbonate to formate has recently been used to reversibly store H₂ at 5–8 MPa and 70 °C (refs 31,47). The decomposition of formic acid is catalysed by numerous homogeneous and heterogeneous transition-metal compounds^{4,21,22,34,38,48–51}. One of the present authors (Y.H.) has reported an iridium catalyst with a rate of 14,000 h^{–1} at 90 °C (ref. 22) and Boddien and colleagues have reported a TON of 92,000 with an iron catalyst at 80 °C (ref. 52). However, all reported high-turnover CO₂ hydrogenation catalysts require prohibitively high pressures and/or temperatures, often ranging from 5 to 6 MPa and 120 to 200 °C, respectively, and in some cases also requiring amine additives. Most importantly, no reported system, including metal-hydride and nanostructured materials, has been successful in reversibly storing H₂ in good yield within the same medium or under mild conditions.

Our approach to hydrogen storage using CO₂ and H₂ is shown in Fig. 1. A water-soluble, pH-modulated catalyst drives the hydrogenation of CO₂ to formate under basic conditions, and hydrogen release is easily triggered by acidifying the solution to protonate the catalyst. Progress has been reported in this regard (Y.H.) using well-defined pH-dependent catalysis with [(Cp*)Ir(dhbp)(OH₂)]SO₄ ([I(OH₂)]SO₄); dhbp = 4,4′-dihydroxy-2,2′-bipyridine; Cp* = pentamethylcyclopentadienide), which is activated once its ‘multifunctional’⁵³ phenolic ligand is deprotonated²⁵. The catalytic rate constant for this varies linearly with the ligand σ -donor power of the substituent on the phenanthroline or

¹Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, USA, ²National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5-2, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, ³The Scripps Research Institute, 130 Scripps Way, Jupiter, Florida 33458, USA,

⁴Department of Natural Science, Baruch College, CUNY, New York, New York 10010, USA. *e-mail: hull@bnl.gov; himeda.y@aist.go.jp; fujita@bnl.gov

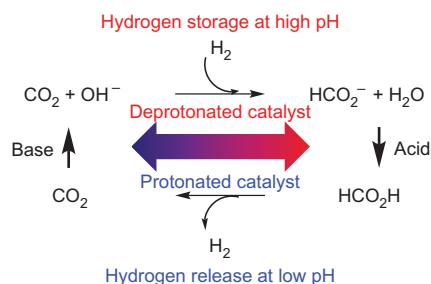


Figure 1 | Reversible H_2 storage is achieved by switching the pH to protonate or deprotonate the catalyst. H_2 is stored by the hydrogenation of CO_2 in the presence of hydroxide (basic aqueous conditions) and then regenerated by the addition of acid. The reductive (red) or oxidative (blue) reactions that interconvert CO_2 , H_2 and $\text{HCO}_2^-/\text{HCO}_2\text{H}$ can be favoured by protonating and deprotonating a proton-responsive catalyst.

bipyridine ligand backbone^{22,24,25,53}. Because $\sigma_{\text{P}^+\text{OH}}^+ = -0.91$ and $\sigma_{\text{P}^+\text{O}^-}^+ = -2.30$, catalysis is greatly enhanced when the ligand is deprotonated to $-\text{O}^-$. Inspired by the use in nature of hydrogen bonds^{54,55} and bases to relay protons in enzyme active sites^{48,55}, we sought to design a catalyst that would create synergy between electronic activation on the one hand, and the pendent-base properties of $-\text{OH}$ or $-\text{O}^-$ on the other, as well as facilitate the interaction of H_2 , CO_2 , H_2O , HCO_2^- , HCO_2H and H^+ in the primary coordination sphere of iridium.

Here, we report the preparation and catalytic activity of $[\text{2Cl}_2]^{2+}$ (Fig. 2a), a dinuclear Cp^*Ir catalyst with 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine (thbpy) as a bridging ligand. $[\text{2Cl}_2]^{2+}$ crystallizes as the chloride salt, but rapidly hydrolyses to $[\text{2}(\text{OH}_2)_2]^{4+}$ and 2Cl^- in water, and may then be deprotonated to $2'(\text{OH}_2)_2$ above pH 5 (Fig. 2b). We observe superior catalytic performance using $2'(\text{OH}_2)_2$ and $[\text{2}(\text{OH}_2)_2]^{4+}$ for storing and releasing H_2 , respectively, under very mild reaction conditions. For CO_2 hydrogenation,

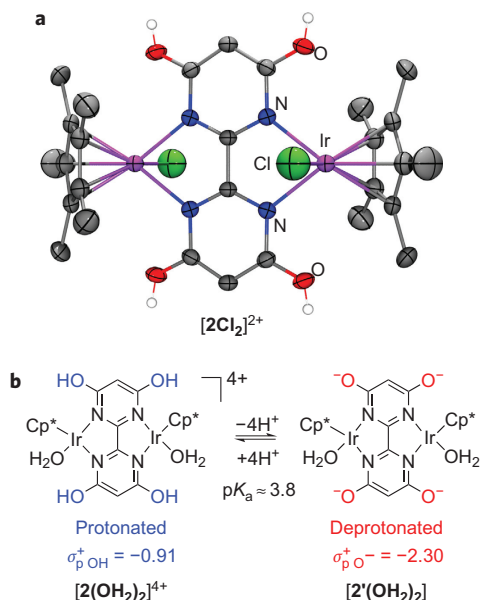
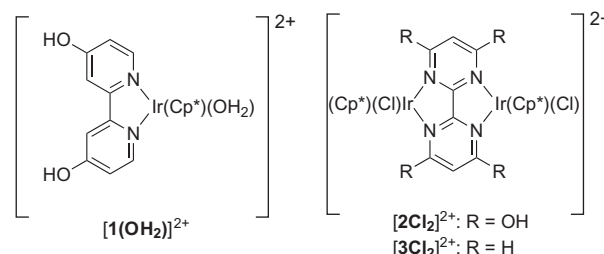


Figure 2 | Crystal structure of $[\text{2Cl}_2]^{2+}$ and reversible formation of $[\text{2}(\text{OH}_2)_2]^{4+}$ and $2'(\text{OH}_2)_2$. **a**, Thermal ellipsoid plot of **2** as $[\text{Ir}(\text{Cp}^*)(\text{Cl})]_2(\text{thbpy})^{2+}$, crystallized from aqueous Na_2SO_4 . C–H bonds are omitted for clarity. **b**, Reversible formation of $[\text{2}(\text{OH}_2)_2]^{4+}$ and $2'(\text{OH}_2)_2$. The pendent $-\text{OH}$ in $[\text{2}(\text{OH}_2)_2]^{4+}$ is 'proton responsive' because it can be deprotonated to $-\text{O}^-$ to give $2'(\text{OH}_2)_2$, where the ligand becomes a strong donor, as indicated by the Hammett parameter $\sigma_{\text{P}^+\text{O}^-}^+$. $[\text{2}(\text{OH}_2)_2]^{4+}$ and $2'(\text{OH}_2)_2$ also have pendent bases close to the metal coordination sphere.

we observe high turnovers at room temperature and ambient pressure, and for the catalytic decomposition of formate the catalytic rate is faster than any previous report ($228,000 \text{ h}^{-1}$). Accordingly, we have realized pH-switchable H_2 storage (as outlined in Fig. 1) with $2'(\text{OH}_2)_2$ and $[\text{2}(\text{OH}_2)_2]^{4+}$ for the first time. We are able to regenerate 2.3 MPa of H_2 following exposure of $2'(\text{OH}_2)_2$ to 0.1 MPa of a 1:1 $\text{H}_2:\text{CO}_2$ mixture at room temperature, and then repeat the cycle. No CO gas impurities are detected, so the purity of the regenerated gas is suitable for use in some H_2 fuel cells, and the temperatures used are also well within fuel cell limits. To validate the role of thbpy in these reactions, we compared the catalytic activity of $[\text{2}(\text{OH}_2)_2]^{4+}$ with the monometallic complex $[\text{1}(\text{OH}_2)_2]^{2+}$ with activating groups but no pendent base, and with $[\text{3Cl}_2]^{2+}$ ($[\text{Ir}(\text{Cp}^*)(\text{Cl})]_2(\text{bpy})^{2+}$, bpy = 2,2'-bipyrimidine), which has no activating groups or pendant bases.



Our preliminary mechanistic studies and theoretical calculations support our hypothesis that the ligand $-\text{OH}$ and $-\text{O}^-$ moieties significantly lower the energy barriers involved in H_2 storage via inner-sphere interactions with H_2 and HCO_2^- .

Results and discussion

Synthesis, structure and characterization of **2.** The thbpy ligand was obtained by reducing 4,4',6,6'-tetramethoxy-2,2'-bipyrimidine, and $[\text{2Cl}_2]\text{Cl}_2$ was prepared by stirring a 1:1 mixture of $[\text{Cp}^*\text{IrCl}_2]_2$ and thbpy in methanol. Layering a methanolic solution of $[\text{2Cl}_2]\text{Cl}_2$ onto concentrated Na_2SO_4 gave air-stable crystals suitable for X-ray diffraction (Fig. 2a). The crystal structure shows two iridium atoms, each coordinated to a Cp^* ligand, a chloride ligand and to two nitrogen atoms of the bridging ligand to form a bimetallic complex. The Ir–N bond lengths are similar to those in $[\text{3Cl}_2]^{2+}$, which was synthesized and compared to $[\text{2Cl}_2]^{2+}$ because it is structurally similar but has no hydroxyl groups. Notably, the monometallic iridium catalyst could not be isolated when $[\text{Cp}^*\text{IrCl}_2]_2$ was used as the limiting reagent, suggesting that the affinity for the second iridium atom is high. The pK_{a} of the thbpy ligand was determined by an acid–base titration through $1 < \text{pH} < 13$ and a least-squares fit to determine the midpoint of the sigmoidal curve (Supplementary Fig. S1). The thbpy ligand in $[\text{2}(\text{OH}_2)_2]^{4+}$ becomes deprotonated in the range $2 < \text{pH} < 5$ with a midpoint at pH 3.8 (ref. 56). Thus $\text{pK}_{\text{a}} = 3.8$ is an indication of the average acid dissociation constant for the thbpy ligand, and $[\text{2}(\text{OH}_2)_2]^{4+}$ and $2'(\text{OH}_2)_2$ exist in their fully protonated and deprotonated forms below pH 2 and above pH 5, respectively. The second midpoint near pH 9.8 (Supplementary Fig. S1 and ref. 56) is assigned to the ionization of $2'(\text{OH}_2)_2 \rightarrow [2'(\text{OH})_2]^{2-} + 2\text{H}^+$, indicating that this species is more basic than the aquo ligand in $1'(\text{OH}_2)$ ($\text{pK}_{\text{a}} = 8.9$).

Catalytic hydrogenation of CO_2 . The catalytic hydrogenation of CO_2 by iridium complexes $[\text{1}(\text{OH}_2)_2]^{2+}$, $[\text{2Cl}_2]^{2+}$ and $[\text{3Cl}_2]^{2+}$ was investigated under a range of conditions (summarized in Table 1). Under the basic conditions investigated, $[\text{1}(\text{OH}_2)_2]^{2+}$, $[\text{2Cl}_2]^{2+}$ and $[\text{3Cl}_2]^{2+}$ exist in water as $1'(\text{OH}_2)$, $2'(\text{OH}_2)_2$ and $[\text{3}(\text{OH}_2)_2]^{4+}$, respectively, due to the rapid hydrolysis of Cl^-

Table 1 | Hydrogenation of CO₂ or bicarbonate (1 M NaHCO₃, pH = 8.4) in H₂O (1:1 H₂:CO₂).

Entry	Catalyst	Pressure (MPa)	Temp. (°C)	Initial TOF [†] (h ⁻¹)	TON	Final [formate] (M)	Ref.
1	[RhCl(η ⁴ -C ₈ H ₁₂) ₂]	4	25	52	1,150	1.55	65
2	RhCl(tppm) ₃	4	24	262	524	–	66
3	Ir(PNP)*	5	200	150,000	300,000	0.6	30
4	Ir(PNP)*	6	120	73,000	3,500,000	0.7	30
5	Ir(PNP)*	5.5	185	14,500	348,000	0.7	27
6	1'(OH ₂) ₂	0.1	25	7	92	0.005	25
7	2'(OH ₂) ₂	0.1	25	64	7,200	0.36	Present
8	2'(OH ₂) ₂ [‡]	0.1	25	70	2,230	0.56	Present
9	2'(OH ₂) ₂ [‡]	4	50	15,700	153,000	1.53	Present
10	2'(OH ₂) ₂ [‡]	5	80	53,800	79,000	0.16	Present
11	2'(OH ₂) ₂ [‡]	3	50	9,400	42,500	1.70	Present
12	2'(OH ₂) ₂	1	50	3,050 [§]	6,100	0.305	Present
13	[3(OH ₂) ₂] ⁴⁺	0.1	25	0	0	0	Present
14	[3(OH ₂) ₂] ⁴⁺	1	50	55 [§]	110	0.006	Present

*PNP-type pincer ligand. [†]Averaged rate for initial 1 h. [‡]Reaction carried out in 2 M KHCO₃. [§]Average rate for the entire reaction. ^{||}Total pressure at room temperature in 1 M KOH (5 ml) and THF (0.1 ml). See cited references for structures. These data, as well as catalyst concentration and reaction times, are shown in Supplementary Table S1.

(see Fig. 3). Entries 1–5 in Table 1 show selected results from other known systems, for comparison. However, good catalyst performance in those systems requires extraordinary pressures (above 5 MPa) and temperatures (120–200 °C). In contrast, when using a 1:1 H₂:CO₂ gas mixture at 0.1 MPa and 25 °C, 2'(OH₂)₂ achieved a turnover frequency (TOF) of 64 h⁻¹ and TON of 7,200, and yielded 0.36 M formate (entry 7, pH 8.1). When 2 M KHCO₃ was used, the final formate concentration was increased to 0.56 M after 216 h and an initial TOF of 70 h⁻¹ was achieved (Table 1, entry 8). This is an improvement of nearly an order of magnitude over our previous report of 7 h⁻¹ for 1'(OH₂)₂ (entry 6), the only other catalyst that is active under ambient conditions (1'(OH₂)₂ and 2'(OH₂)₂ are compared in Supplementary Fig. S2). The

reaction rate varies linearly with the concentration of 2'(OH₂)₂ (10–100 μM), indicating a first-order dependence (Supplementary Fig. S3). Rates and turnovers for 2'(OH₂)₂ were increased to a TOF of 53,800 h⁻¹ and TON of 153,000 under pressurized conditions at relatively low temperature (Table 1, entries 9 and 10), resulting in a high concentration of 1.70 M formate solution (Table 1, entry 11). In comparison, [3(OH₂)₂]⁴⁺ shows no reaction at room temperature after 8 h (Table 1, entry 13), and only 110 turnovers under pressurized conditions (entry 14, *T* = 50 °C, *P* = 1 MPa, 2 h). The difference between the reaction rates of catalysts 2'(OH₂)₂ and [3(OH₂)₂]⁴⁺ clearly illustrates the effect of the ligand on the rate of catalytic CO₂ hydrogenation. Further investigations of the electronic effects that may contribute to this reaction are under way.

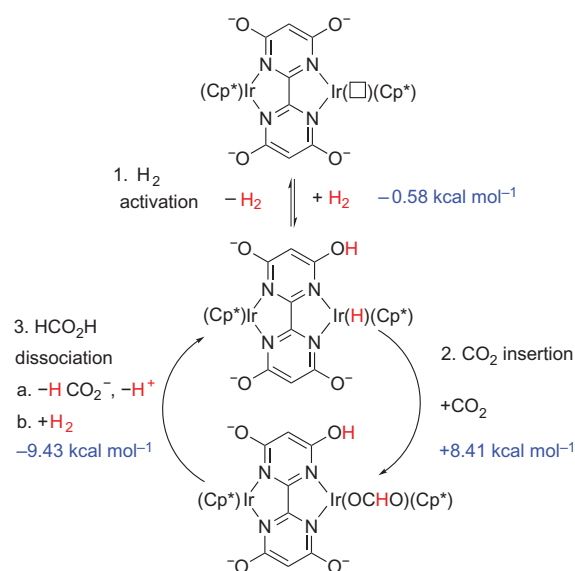


Figure 3 | Proposed mechanism and gas-phase free energy calculations for 2'(OH₂)₂ after it loses protons and water. (1) Activating H₂ and forming a metal hydride; (2) inserting CO₂ into the Ir–H bond; (3a) eliminating formate and a proton; and (3b) adding H₂ to regenerate the hydride. The free-energy changes in kcal mol⁻¹ at pH 8.4 (Δ*G*[°]) are indicated in blue. Only one iridium site is illustrated for clarity. See Supplementary Fig. S8 for the ¹H NMR spectrum of the Ir–H species, and Supplementary Figs S9 and S10 for theoretical details and the plotted free-energy surface. All energies are relative to the species indicated by an open square, which indicates a vacant coordination site, that is, after dissociation of the OH₂ or OH⁻ ligand.

Retrieving H₂ from formic acid. Having established that 2'(OH₂)₂ efficiently converts CO₂ to aqueous formate under basic conditions, we examined the release of H₂ under acidic conditions. The results are summarized in Table 2. Under optimal reaction conditions (pH 3.5) the catalyst is intermediately protonated between [2(OH₂)₂]⁴⁺ and 2'(OH₂)₂, and denoted 2*(OH₂)₂. 2*(OH₂)₂ catalyses the release of H₂ and CO₂ (1:1) from aqueous HCO₂H/HCO₂Na mixtures at a TOF of 228,000 h⁻¹ at 90 °C and TON of 308,000 at 80 °C, the highest TOF and TON yet reported (Table 2, entries 2 and 5). This performance is superior even to catalysts that require organic additives^{35,42}. The liquid-to-gas conversion is quantitative in all cases, regardless of whether HCO₂H or HCO₂Na is used, although the latter is significantly slower (Supplementary Fig. S4.) Surprisingly, [3(OH₂)₂]⁴⁺ and 2*(OH₂)₂ generated H₂ from formate at similar rates at 60 °C (Table 2, entry 6). This suggests that the hydroxyl groups on the ligand have a larger effect in the hydrogenation of CO₂ than they do for the dehydrogenation of formic acid (see the mechanism in Fig. 3).

We also investigated the rate of H₂ evolution as a function of pH (Fig. 4). The rate peaks at 31,600 h⁻¹ at pH 3.5, which is close to the *pK_a* of the catalyst (*pK_a* = 3.8) and to the *pK_a* of formic acid (*pK_a* = 3.75). These data, combined with the similar rates for [3(OH₂)₂]⁴⁺ and 2*(OH₂)₂, suggest the ligands play different roles in the hydrogenation and dehydrogenation reactions. A thorough mechanistic investigation is under way.

pH-switchable consumption or production of H₂. Despite years of research, only two examples of reversible H₂ storage—that is, a system that starts with H₂, stores it, and subsequently regenerates H₂—have been reported. However, both systems required pressures of 8–10 MPa, and in one example the solvent had to be

Table 2 | Catalytic decomposition of HCO₂H by 1, 2 and 3.

Entry	Catalyst	Catalyst conc. (μM)	Temp. (°C)	Time (h)	Initial TOF [†] (h ⁻¹)	TON	Final [HCO ₂ H] (M)
1	[1(OH ₂) ₂] ^{2+‡}	200	60	4	2,400	5,000	0
2	2*(OH ₂) ₂ [‡]	50	60	4	12,000	20,000	0
3	2*(OH ₂) ₂	50	60	18	31,600	16,800	0.16
4	2*(OH ₂) ₂	1.5	80	12	158,000	308,000	0.54
5	2*(OH ₂) ₂	3.1	90	7	228,000	165,000	0.48
6	[3(OH ₂) ₂] ⁴⁺	50	60	1.5	32,000	10,000	0.50

Reaction conditions: 1 M HCO₂H/HCO₂Na (1:1, pH 3.5). [†]Averaged rate for initial 5–15 min. [‡]1 M HCO₂H. 2*(OH₂)₂ indicates that the thbpy ligand on 2 is intermediately protonated between [2(OH₂)₂]⁴⁺ and 2(OH₂)₂ under the reaction conditions. See main text for details.

evaporated to reverse the reaction^{31,47}. The proposal shown in Fig. 1 is unique, because pH, a well-defined and low-energy trigger, controls H₂ storage or production.

In a proof of concept study following Fig. 1, we exposed 2'(OH₂)₂ in 2 M KHCO₃ (20 ml) to a constant flow of a 1:1 CO₂:H₂ gas mixture at ambient pressure for 136 h to yield 0.48 M formate (Table 3, cycle 1). The reaction solution was then cooled and adjusted to pH 1.7 with 4 M sulfuric acid to protonate the catalyst to [2(OH₂)₂]⁴⁺. H₂ release was subsequently triggered by warming the solution in the glass autoclave to 50 °C, and resulted in a final closed-system pressure of 2.3 MPa of H₂/CO₂ (1:1), with no detectable CO by-product (Supplementary Fig. S5). Thus, pressure does not inhibit H₂ regeneration, an essential feature in using stored H₂ as a fuel¹⁰. The cycle was then repeated by cooling the system and adjusting the pH with KHCO₃. The system is therefore recyclable, and the catalyst does not need to be isolated before reuse. To our knowledge this is the first system—including metal organic frameworks, tank systems and other metal hydrides—that is capable of storing H₂ and creating a pressurized H₂ system under mild conditions^{31,57}. Further efforts to optimize this storage process are ongoing. The exact experimental conditions are listed in the Supplementary Information, together with an additional scheme for the reaction cycle and a picture of the test vessel (Supplementary Figs S6 and S7, respectively).

Preliminary mechanism for CO₂ reduction. We hypothesized that introducing a ligand –OH moiety on [2(OH₂)₂]⁴⁺ would, via 2'(OH₂)₂, act as a base on an electronically activated catalyst. This is because H₂ would be activated by a proton relay^{49,55}, and because the Ir–H of 2'(H)₂ would be an excellent nucleophile for attack at CO₂ due to the high σ-donor power of the four –O[–] groups^{15,27}.

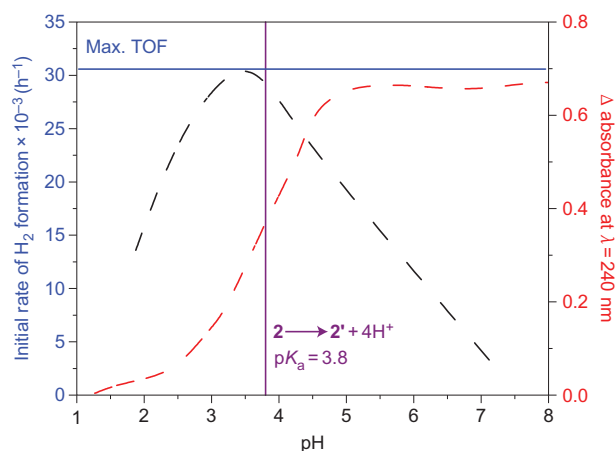


Figure 4 | Variation of the rate of H₂ evolution (left y-axis, blue) with pH compared to the ionization of the thbpy ligand (right y-axis, red). The mid-ionization point for [2(OH₂)₂]⁴⁺ to 2'(OH₂)₂ is indicated in purple, and the maximum TOF is shown in blue. See the main text for a discussion of this trend.

This is shown in steps 1 and 2 of Fig. 3. Our calculations and preliminary mechanistic experiments support this hypothesis, as does the experimentally determined absence of hydrogenation activity with [3(OH₂)₂]⁴⁺ described above. Water (or OH[–]) replaces Cl[–] as a ligand to iridium at a rate faster than could be measured by hand mixing experiments, and therefore [3(OH₂)₂]⁴⁺ is the starting complex before H₂ or CO₂ coordinate iridium.

An iridium hydride was easily formed experimentally with H₂ gas near room temperature and confirmed by the ¹H NMR singlet at –10.7 ppm in the ¹H NMR spectrum (Supplementary Fig. S8) by exposing 2'(OD₂)₂ to an atmosphere of H₂. A long T₁ relaxation time of 3,700 ms at 20 °C for the hydride singlet unambiguously indicates that a classical metal-hydride-type complex is formed in the presence of H₂ (ref. 58). Indeed, heterolytic cleavage of H₂ is known to be assisted by pendent bases in iridium complexes⁵⁵. Bubbling H₂ through a solution of 2'(OH₂)₂ at basic pH caused shifts in the UV–visible spectrum from λ_{max} = 335 nm to λ_{max} = 328 nm at room temperature, followed by a shift to λ_{max} = 342 nm when CO₂ was bubbled through the same solution. These data are consistent with the standard mechanism for similar catalysts, which is (1) formation of an Ir–H species once H₂ displaces OH₂, followed by (2) insertion of CO₂ to give a formate complex, and (3) subsequent regeneration of the hydride with dissociation of formate or formic acid. Importantly, dissolved CO₂ was essential for formate production, and a very small amount of the product formed when only bicarbonate was used (Table 1). We therefore propose that CO₂ and not bicarbonate is reduced by 2'(OH₂)₂. The higher yield of formate in the presence of bicarbonate may therefore be due to the increased presence of dissolved CO₂, due to Le Chatelier's principle.

The calculated free energies of these intermediates adjusted for pH 8.4 in the gas phase are shown in Fig. 3, consistent with the experimental data in Table 1, and are plotted in Supplementary Fig. S10 (see Methods and Supplementary Information for theoretical details and energy tables). The formation of Ir–H in step 1 of Fig. 3 is slightly exoergic (ΔG^o = –0.58 kcal mol^{–1}), consistent with our proton-relay picture. Because pH 8.4 > catalyst pK_a, it is unlikely that the ligand remains protonated, and we cannot rule out the participation of bulk OH[–] (ref. 59). The most endoergic step (ΔG^o = +8.41 kcal mol^{–1}) is CO₂ insertion into the Ir–H species (Fig. 3, step 2), seems rate limiting in these calculations

Table 3 | H₂ storage cycles according to Fig. 1.

Cycle	Hydrogenation of CO ₂		Decomposition of formic acid		
	Time (h)	Generated formate (M)	Time (h)	Gas produced (MPa)	Formic acid remaining (M)
1	136	0.48	8	2.34	0.017
2	182	0.38	8	1.93	0.024

Hydrogenation reaction: 2'(OH₂)₂ dissolved in 2 M KHCO₃ under a constant flow of a 1:1 CO₂:H₂ at 0.1 MPa and 30 °C. Decomposition in a closed high-pressure vessel with [2(OH₂)₂]⁴⁺ at pH 1.7 and 50 °C. Experimental procedures are described in the Supplementary Information.

(supported by work by Fukuzumi and colleagues⁶⁰). In contrast to Nozaki's and Hazari's catalysts^{27,59,61}, step 3 (displacing formate with H₂ to regenerate the Ir–H species) is moderately exoergic in our system ($\Delta G^\circ = -9.43$ kcal mol⁻¹). The net ΔG° for the catalytic cycle is -1.60 kcal mol⁻¹, and the relatively flat free energy profile in this catalytic cycle may explain the superior catalytic activity of 2'-(OH₂)₂ at room temperature. Although our calculations involve the reaction of only one of the iridium atoms, we expect that having two metal centres will increase the rate of catalysis⁶². Transition-state calculations for the consumption and production of H₂ will be presented in forthcoming work.

Summary and conclusion

We report the synthesis and characterization of [2(OH₂)₂]⁴⁺, the first catalyst capable of reversible H₂ storage using CO₂ in aqueous media under mild temperatures and pressures. A recyclable pressurization sequence demonstrates that low-pressure (atmospheric) H₂ gas can be stored as liquid formate, and then used to regenerate high-pressure H₂ and CO₂ for possible fuel applications. The –OH moieties on the thbpy ligand are pH-responsive, and H₂ storage can be turned on or off by adjusting the pH of the solution. CO₂ hydrogenation is facilitated because, in addition to electronically activating the catalyst, the –O⁻ in 2'-(OH₂)₂ facilitates H₂ heterolysis by acting as a pendant base. Rates as high as 70 h⁻¹ (25 °C and 0.1 MPa) and 53,800 h⁻¹ (80 °C and 5 MPa) are observed. [2(OH₂)₂]⁴⁺ decomposes formic acid or formate to give CO-free H₂ and CO₂ at low pH. We observe a TOF of 228,000 h⁻¹ at 90 °C and TON of 308,000 at 80 °C, the highest TOF and TON yet reported. Detailed mechanistic and theoretical studies are in progress, as well as an investigation into H₂ formation from formate.

Methods

General. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques or in a glovebox, and all aqueous solutions were degassed before use. ¹H NMR and ¹³C NMR spectra were recorded on Varian INOVA 400 and Bruker Avance 400 and 500 spectrometers using sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS sodium salt) as an internal standard. The X-ray structure was determined using a Bruker Kappa Apex II diffractometer. pH values were measured on an Orion 3-Star pH meter with a glass electrode after calibration to standard buffer solutions. The evolved gas was measured at various intervals by a gas meter (Shinagawa Corp., W-NK-05). H₂ was detected by a thermal conductivity detector using an activated 60/80 carbon column, and CO₂ and CO were detected using a flame ionization detector equipped with a methanizer using a Porapak Q 80/100 column at 50 °C on a GL Science GC390 gas chromatograph. Formate was produced from research-grade CO₂ (>99.999%) and H₂ (>99.9999%), or mixed gas (CO₂/H₂ = 1/1) through an O₂ trap. Formate product concentrations were monitored by high-performance liquid chromatography on an anion-exclusion column (Tosoh TSKgel SCX(H⁺)) using aqueous H₃PO₄ solution (20 mM) as eluent and a ultraviolet detector ($\lambda = 210$ nm). [Cp*IrCl₂]₂ was prepared by refluxing a suspension containing a 2:1 mixture of hydrated IrCl₃·Cp* in methanol for 48 h (ref. 63). Complexes [1(OH₂)₂]²⁺ (ref. 24) and [3Cl₂]²⁺ (ref. 62) were prepared according to literature procedures. The synthetic procedures and characterization of the thbpy ligand and [2Cl₂]²⁺, as well as procedures for the uptake and regeneration reactions, are described in the Supplementary Information. Density functional theory calculations were performed using the Gaussian 09 software package⁶⁴ with the B3LYP functional and a CEP-121G basis set for iridium, and 6-31 + G(d,p) for C, N, O and H, and are described in detail in the Supplementary Information.

Received 22 September 2011; accepted 6 February 2012;
published online 18 March 2012

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Acknowledgements

The work at Brookhaven National Laboratory is funded under contract DE-AC02-98CH10886 with the US Department of Energy and supported by its Division of Chemical Sciences, Geosciences, & Biosciences, Office of Basic Energy Sciences. J.F.H. acknowledges support as a BNL Goldhaber Distinguished Fellow. Y.H. acknowledges support from the Japanese Ministry of Economy, Trade, and Industry. R.P. and B.H. were supported by the CCHF 101 (grant no. DE-SC0001298).

Author contributions

J.F.H. and Y.H. conceived the project, carried out the bulk of the experimental work and wrote the manuscript. W.W. made significant contributions to the synthesis and characterization. R.P. and B.H. provided the thbpy ligand. D.J.S. solved the crystal structure. J.T.M. carried out theoretical work and E.F. oversaw all work.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/naturechemistry. Reprints and permission information is available online at <http://www.nature.com/reprints>. Correspondence and requests for materials should be addressed to J.F.H., Y.H. and E.F.