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Base-free reversible hydrogen storage using a tethered π -coordinated-phenoxy ruthenium-dimer pre-catalyst

Raphael Verron,[†] Emmanuel Puig,[‡] Pierre Sutra,[‡] Alain Igau,^{*‡} and Cédric Fischmeister^{*†}

[†]Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226

F-35042 Rennes, France. E-mail : cedric.fischmeister@cnrs.fr

[‡] CNRS, LCC (Laboratoire de Chimie de Coordination). Université de Toulouse, UPS, INPT.

205 route de Narbonne, 31077 Toulouse Cedex 4, France. E-mail: alain.igau@lcc-toulouse.fr

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ABSTRACT: A dimeric tethered π -coordinated-phenoxy ruthenium pre-catalyst has been used for the base-free hydrogenation of CO₂ in DMSO. The same pre-catalyst was also efficient in the reverse dehydrogenation of formic acid yet under base-free conditions. An unprecedented base-free cycle consisting in hydrogen storage and release was successfully implemented with the same pre-catalyst. The latent property of the catalyst has been introduced in the concept of hydrogen storage/transportation/release

DEDICATION: This work is dedicated to the memory of Prof. I. T. Horváth

INTRODUCTION

The hydrogen economy based on hydrogen as a carbon-free energy vector has its roots in the second part of 20th century¹ but the fossil era with its abundant and low cost resources has overshadowed this domain until recently. Indeed, environmental issues and depletion of fossil resources have changed the energy supply situation and new sources of carbon-free energy are urgently needed. Hydrogen is one of the options foreseen to supply energy to future generations but some challenges need to be tackled in order to ensure its development. Among these challenges, the production, handling, storage and transportation are major concerns. Regarding storage, hydrogen can be stored as compressed gas ($100 < P < 700$ bar) or liquefied ($T = -253$ °C)² but both methods are energy intensive, require advanced storage materials and equipment and raise safety concerns. Metal-hydrides (MgH_2 , $NaBH_4$, $LiNH_2$...) are possible storage materials but they suffer from low storage capacity and slow storage and release kinetics. Advanced metal-hydride materials (nanostructured, reactive hydride composites, alloys, MOFs) are therefore under investigations.³ Beside those options, the chemical storage of hydrogen using Liquid Organic Hydrogen Carriers (LOHCs) is very appealing as most of these chemicals are non-toxic, and easy to handle and to transport.⁴ In this context, formic acid appears as a good candidate to store hydrogen in a reversible manner under mild conditions of pressure and temperature.⁵ Not only is formic acid a stable and not very hazardous liquid, easy to handle and transport (compared to other chemicals in particular mineral acids transported by roads or seas), but its hydrogen content (4.4 wt% or 53 g.L^{-1}) is higher than that of compressed hydrogen (16 g.L^{-1} at 200 bar or 40 g.L^{-1} at 700 bar). Numerous homogeneous⁵ and heterogeneous catalysts⁶ have been reported for the hydrogenation of CO_2 and for the dehydrogenation of formic acid. Many of these catalysts achieved high TONs and TOFs in the presence of additives, in particular basic additives, to

promote the catalytic reaction.^{7,8} Basic media could be necessary to assist catalyst turnovers or to make the reaction thermodynamically favorable (CO₂ hydrogenation : $\Delta_r G^0 > + 7.6 \text{ kcal.mol}^{-1}$ in the absence of base vs $-2.3 \text{ kcal.mol}^{-1}$ in the presence of NH₃ in the gas phase).⁹ The stability of catalysts and catalytic species including metal-hydride species under acidic conditions is also a major issue. If basic additives are required to ensure (high) catalytic activity and productivity, their use has an obvious negative environmental and economic impact which could be further amplified if additional purification are required to remove trace amounts of bases which could be prohibitive for downstream applications. It should also be noted that under basic conditions in aqueous media, the couple bicarbonate/formate constitutes another possibility for hydrogen storage.¹⁰ To date, only very few homogeneous catalysts have been reported for the base- or additive-free hydrogenation of carbon dioxide¹¹ and formic acid dehydrogenation.¹² Over the past 40 years, archetypal bifunctional catalysts such as the Shvo catalyst,¹³ the Noyori catalyst¹⁴ and, more recently, pincer-type catalysts¹⁵ have been used in homogeneous hydrogenation and dehydrogenation catalysis, sometimes in the absence of a base due to metal-ligand cooperation.¹⁶ In 2014, a new family of 6-membered ring ruthenium complexes featuring Shvo-catalyst similarities was reported by Igau¹⁷ and their catalytic activity under base-free conditions was very recently demonstrated in the reduction of ketones under hydrogenation and transfer hydrogenation conditions using either *i*-propanol or formic acid as hydrogen donors (Figure 1).¹⁸ In particular, a Shvo-type reactivity was demonstrated by the ability of such complex to split H₂ into a ruthenium-hydride with keto-ligand protonation. As part of the ongoing efforts on the implementation of LOHC in homogeneous catalysis^{12h,19} we have investigated the potential of these tethered-ruthenium catalysts for CO₂ hydrogenation and the reverse dehydrogenation of formic acid, both performed under base-free conditions.

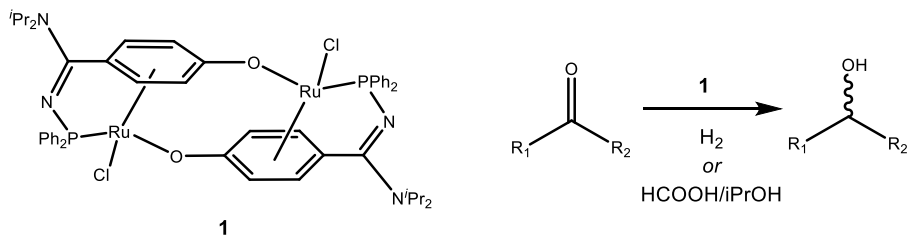


Figure 1 Tethered ruthenium-dimer pre-catalyst **1**

RESULTS AND DISCUSSION

CO₂ hydrogenation

The hydrogenation of CO₂ into formic acid (Fig. 2) has been scarcely reported under base-free conditions since the early reports by Khan^{11a} and Nicholas.^{11b} In the absence of base, this reaction is thermodynamically feasible if entropic contribution is improved through solvation of CO₂, H₂ and formic acid using appropriate solvents, of which DMSO was proved the most suitable with ruthenium catalysts (Fig. 2).^{11c,e-h} It should be noted that ruthenium catalysts lead to moderate TONs (< 500), excepted for the study reported by Leitner where a TON of 4200 was achieved at high pressure (120 bar). Beside ruthenium, iridium was found competent for this transformation carried out in water.^{11h} Studies focused on process development were also recently reported.²⁰

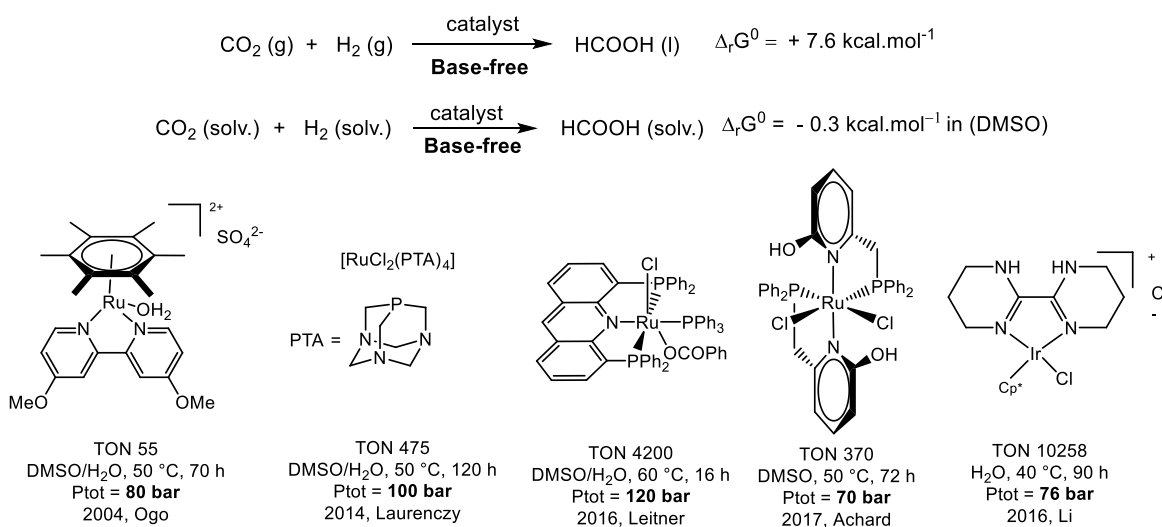


Figure 2 Active complexes in the catalytic hydrogenation of CO₂ under base-free conditions

We initiated our studies on the hydrogenation of CO₂ using DMSO as solvent at 60 °C with a total pressure of 40 bar (20 H₂ / 20 CO₂). We were pleased to observe the formation of formic acid though in a low concentration (3.2 10⁻² M) corresponding to a TON of 9 (Table 1, entry 1). This value could be increased to 105 upon increasing the total pressure to 60 bar, still with equal partial pressures of dihydrogen and carbon dioxide. In contrast with the results obtained by Leitner,^{11f} we observed a slight decrease of the TON when a 95/5 mixture of DMSO/ water was used as solvent (Table 1, entry 3). In the same manner, an excess of hydrogen did not bring any improvement as sometimes observed (Table 1, entry 4). Maintaining the total pressure at 60 bar, the TON could be further improved by increasing the reaction temperature from 60 °C to 80 °C thus indicating that equilibrium was not reached after 17 h at 60 °C (Table 1, entries 2 and 5). Indeed, the hydrogenation of CO₂ being exothermic, an increase of temperature should translate in a lower TON.^{11e,h} Increasing further the temperature resulted in a lower TON of 90 which could also be due to a lower stability of the catalyst at this higher temperature, (Table 1, entry 6). Eventually, the highest TON was obtained at 70 bar over a reaction time of 65 h (Table 1, entries 7, 8). These results demonstrate that complex **1** is competent for the CO₂ hydrogenation and open the way for improvements through ligand modification owing to the numerous possibilities offered by the structure of **1**. It is also important to mention that those results were obtained under relatively low pressure.²¹ For example, Leitner obtained the highest TON at a total pressure of 120 bar^{11f} and the analysis of the [HCOOH]_{DMSO} = f(P) in Laurenczy's 2014 seminal report reveals an increase of about a factor 3-4 in TON when increasing the pressure from 60 to 100 bar.^{11e} At 60 bar, 50 °C and after 120 h, a [HCOOH] ≈ 0.5 M was obtained, which is comparable to our best result obtained at 60 bar (Table 1, entries 7, 8).

Table 1 Catalytic hydrogenation of CO₂ with **1**^a

| Entry | Solvent | P _{CO₂} ^c | P _{H₂} ^c | T (°C) | t (h) | [FA] (mol.L ⁻¹) ^d | TON ^{e,f} |
|-------|------------------------------------|--|---|--------|-------|--|----------------------|
| 1 | DMSO | 20 | 20 | 60 | 17 | 3.2 10 ⁻¹ | 9 |
| 2 | DMSO | 30 | 30 | 60 | 17 | 3.6 10 ⁻¹ | 105(12) ^g |
| 3 | DMSO/H ₂ O ^b | 30 | 30 | 60 | 17 | 2.2 10 ⁻¹ | 58 |
| 4 | DMSO | 20 | 40 | 60 | 17 | 2.8 10 ⁻¹ | 73 |
| 5 | DMSO | 30 | 30 | 80 | 17 | 4.5 10 ⁻² | 114 |
| 6 | DMSO | 30 | 30 | 90 | 17 | 3.2 10 ⁻¹ | 90 |
| 7 | DMSO | 35 | 35 | 60 | 17 | 4.5 10 ⁻¹ | 116 |
| 8 | DMSO | 30 | 30 | 60 | 65 | 6.4 10 ⁻¹ | 160 |

^a **1** (5.55 · 10⁻⁶ mol, n(Ru)=1.11 · 10⁻⁵ mol), DMSO (3 mL), 17 h. ^b 2.85 mL/0.15 mL (95/5). ^c at room temperature. ^d determined by NMR using concentration calibration, see ESI. ^e mole of CO₂ or H₂ converted per mole of Ru. ^f average of 2 runs with less than 10% difference. ^g TON at 6 h.

Formic acid dehydrogenation

Contrary to CO₂ hydrogenation into formic acid, the dehydrogenation of formic acid was abundantly reported in the last few years.^{22,23} However, as for CO₂ hydrogenation, examples of base-free dehydrogenation of formic acid are scarce and mostly conducted with iridium catalyst.^{12,24} In this domain, we reported an iridium-based catalyst able to dehydrogenate a 3 M aqueous solution of formic acid with a TOF of 38236 h⁻¹ at 100 °C.^{12h} The catalyst could also dehydrogenate neat formic acid with a TOF of 9174 h⁻¹ at 90 °C. With ruthenium, the very few examples reported employed pre-formed hydride complexes often prepared under basic conditions.^{12f,i} Recently, Milstein reported such a ruthenium-hydride catalyst promoting the dehydrogenation of neat formic acid with a TOF of 2186 h⁻¹ at 95 °C.²⁵ DMSO was chosen as solvent for the dehydrogenation of commercial grade formic acid with **1** (see ESI) at 90 °C, as one

of the objectives of this study was to address the reversibility of the process in a tandem experiment (H₂ storage and release cycle), therefore, both reactions must be conducted in the same solvent. Thus, using a loading of 0.5 mol% in **1** and a formic acid concentration of 2.4 mol.L⁻¹, a TOF of 202 h⁻¹ was obtained and the dehydrogenation which started immediately upon heating was completed in 25 minutes (conv. = 95%, Table 2, entry 1). The catalyst loading could be decreased to 0.25 mol% and high TON (173) could be reached upon extended reaction time, thus emphasizing the robustness of the pre-catalyst **1** and of the active catalytic species (Table 2, entry 2). The effect of formic acid concentration was also scrutinized. High concentrations are desired as they translate into higher volumetric energy content but they are not always tolerated by the catalysts for stability or solubility reasons. As depicted in Table 2, we were pleased to observe a slightly higher initial activity and similar productivity upon doubling the initial formic acid concentration (Table 2, entry 3). Unfortunately, attempts to dehydrogenate neat formic acid were not conclusive. Although commercial grade formic acid contains water, the effect of water on the catalyst efficiency was evaluated and moderate inhibition was observed (Table 2, entry 4). This is of practical and economical interest as anhydrous solvent is thus not necessary.

Table 2 Catalytic dehydrogenation of formic acid with **1**^a

| Entry | Solvent | Catalyst (mol%) | Conv (%) | t (min) | TOF (h ⁻¹) ^b | TON ^b |
|----------------|------------------------------|-----------------|----------|---------|-------------------------------------|------------------|
| 1 | DMSO | 0.5 | 95 | 20 | 202 | 95 |
| 2 | DMSO | 0.25 | 86 | 150 | 84 | 173 |
| 3 ^c | DMSO | 0.5 | 95 | 20 | 234 | 97 |
| 4 | DMSO/H ₂ O (95/5) | 0.5 | 83 | 30 | 132 | 83 |

^a Formic acid (100 μL, 2.65.10⁻³ mol), **1** (14 mg, 1.33.10⁻⁵ mol), solvent (1 mL, [FA] = 2.65 mol. L⁻¹). ^b TOF determined at 10 minutes from gas volume generated. TON determined from gas volume generated. ^c [FA] = 5.3 mol.L⁻¹

Following these promising results, a number of important features has been investigated. First, the purity of the gas released by the reaction was studied since formic acid dehydration may occur as a side reaction releasing CO which is a poison for Proton Exchange Membrane (PEM) fuel cell electrodes.²⁶ CO levels as low as 5-15 ppm were reported to lead to fuel cell degradation.²⁷ It should however be noticed that recent progress were made in CO-tolerant PEM fuel cells.²⁸ The experimental setup consisting in a reaction flask connected to a digital flowmeter was therefore completed by a GC chromatograph equipped with a catharometer detector at the flowmeter outlet. This configuration allowed the nature of the gas released to be followed from the start of the reaction to its completion, bearing in mind that alteration of the catalyst during the dehydrogenation process could alter its selectivity and thus potentially favour dehydration of formic acid. By monitoring the nature of the gas produced under the conditions of Table, 1, entry 1, we could not detect any CO in the gas stream throughout the reaction (detection limit < 1 ppm). Another important issue to address is the capability of the catalyst to generate high pressure of H₂/CO₂ mixture considering that high pressure is of practical utility for downstream applications but also considering that this reaction is reversible. For this purpose, a 22 mL Parr reactor was loaded with 1 mL of formic acid and 14 mg of **1** (0.05 mol%) and then heated at 90 °C in an oil bath. We were pleased to record a pressure increase up to 42 bar, sufficient to supply a flow of hydrogen to PEM-fuel cell.²⁹

To complete the study on FA dehydrogenation, the latent (sometimes quoted dormant) behaviour of complex **1** was evaluated. To our knowledge, this feature, or property, has not been reported in the domain of formic acid dehydrogenation. Latency is the capability of a catalyst to be inactive in the presence of a reagent, typically in the dark and at room or moderately low temperature. Catalytic activity can then be triggered by an external stimulus such as heat, light, mechanical or chemical activation.³⁰ In this way, formulations incorporating the solvents, reagents and the

dormant catalyst can be supplied to end-users who can directly implement the desired catalytic transformation using any of the aforementioned stimuli, thus avoiding the catalyst/reagent mixing step. We believe that this functionality could be exploited in the field of hydrogen storage to make the use of formic acid as a practical and easy to implement LOHC. However, major challenge with latent catalysts concerns their stability upon storage with the reagent and this is particularly true with an acidic reagent such as formic acid. The stability and latent behaviour of **1** were evaluated as follows. Two samples of concentrated formic acid (5.3 M in DMSO) and **1** (0.5 mol%) were prepared under inert atmosphere and stored for 70 h either at room temperature (c.a. 20 °C) or in a fridge (c.a. + 4 °C). Following this storage period some pressure had developed in the storing vial indicating that some dehydrogenation occurred during storage. However, when both samples were submitted to the dehydrogenation procedure, 82% and 93% of the theoretical gas volume was generated, respectively, hence demonstrating that only little dehydrogenation occurred during the storage period. It should also be noted that in both cases, ¹H NMR analyses showed that no formic acid remained in solution after the gas evolution had stopped. These results highlight the potential utilisation of **1** as a latent catalyst although improvements of dormant properties are necessary. Last but not least, these results also demonstrate the stability of complex **1** and the ruthenium species generated upon storage for several hours in a formic acid solution.

Catalytic tandem hydrogenation/dehydrogenation

Having demonstrated the ability of complex **1** to promote both the base-free hydrogenation of CO₂ and the base-free dehydrogenation of formic acid in independent experiments, we turned our attention to the carbon-neutral base-free hydrogen storage and release cycle (Figure 3) which is the basis of a hydrogen battery.

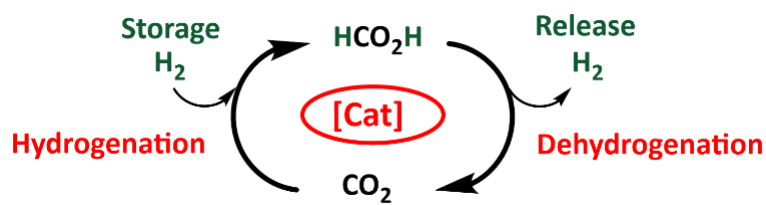


Figure 3 Carbon-neutral hydrogen storage and release principle

Since Leitner's pioneering results on the reversibility of the rhodium-catalysed hydrogenation of CO_2 to formic acid in acetone/ NEt_3 ,³¹ very few catalysts active in these two reactions have been reported, and when they have, the two reactions were carried out independently and always under basic conditions.³² Examples of hydrogen storage and release cycles are even more rare and they were also conducted under basic conditions,³³ sometimes with addition of base between cycles^{32a} or pH adjustments to trigger reversibility.^{32b} During the preparation of this manuscript, Beller reported the reversible hydrogenation of carbon dioxide to formate using a pincer-manganese catalyst in the presence of Lysine or potassium Lysinate for efficient retention of CO_2 .³⁴ With these considerations in mind, we investigated the ability of complex **1** to perform a CO_2 hydrogenation/formic acid dehydrogenation cycle. For this purpose, CO_2 hydrogenation was carried out in a high pressure reactor with complex **1** under the experimental conditions previously described (Table 1, entry 2) leading to the formation of formic acid with a concentration of 4.10^{-1} mol. L^{-1} (Figure 4, **A**). This solution was then transferred to the dehydrogenation setup and immediately heated at $90\text{ }^\circ\text{C}$. This resulted in the release of e.g. 48 mL of gas over 40 minutes corresponding to 94% of the theoretical volume accessible (Figure 4, **B**). The full consumption of formic acid was confirmed by ^1H NMR analysis of the remaining solution. To our knowledge, this base-free hydrogen and release cycle has not been reported before.

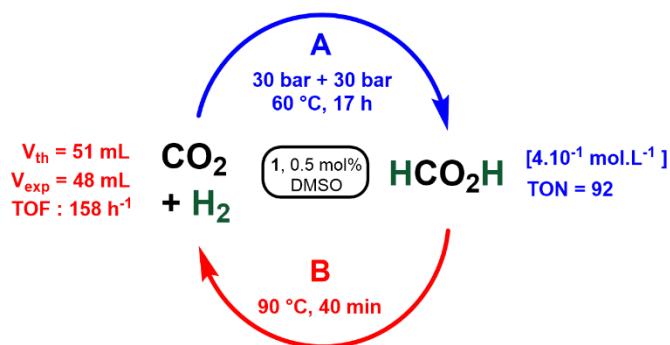


Figure 4 Neutral-carbon hydrogen storage and release with **1**

To further investigate the possibility of cyclic operation with **1**, the reaction was further studied over 5 days on several consecutive hydrogen storage and release cycles. A high pressure reactor was loaded under standard conditions with **1** ($5.7 \cdot 10^{-3}$ mmol) dissolved in DMSO (3 mL) and then pressurized with 30 bar CO_2 + 30 bar H_2 . After stirring for 16-21 h at 60 °C (charge), the reactor was gently cooled down to room temperature and the pressure slowly released. The reactor was then connected to the flowmeter and heated at 90 °C. The gas evolution was immediate and the total volume released was consistent with the cycle described earlier (Figure 4). As depicted in Figure 5, the two first cycles could be performed with similarly high gas volume released depending on the hydrogenation duration (charge) before a slight decrease was observed in the next third and fourth cycles where longer dehydrogenation times (discharge) were necessary to release lower amounts of gas. Despite this decrease of performances over several cycles, this study is a solid evidence of the robustness of the active catalytic species involved in the hydrogen storage and release process with **1**. It is of great importance to note that after the 4th run, the reaction medium remained perfectly clear and homogeneous without any trace of insoluble solid residue. Furthermore, the previously reported reactivity studies performed under stoichiometric conditions

and diverse experimental conditions (HCl, MeOTf, Br(CH₂)₂OTf, TIPF₆, H₂) did not evidence the possible formation of nanoparticles.¹⁷

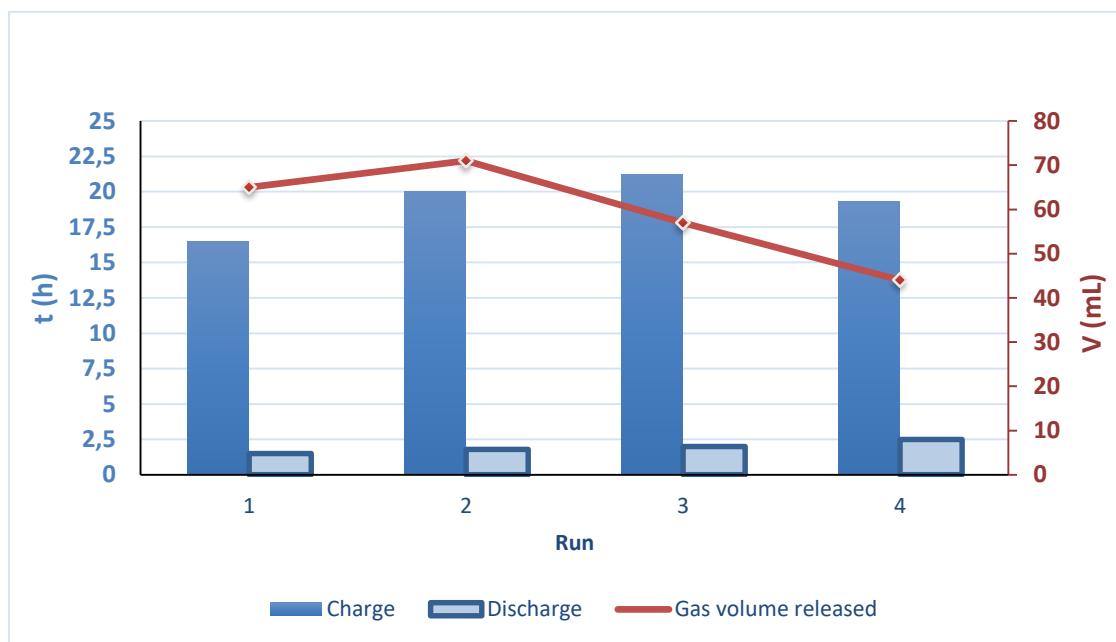
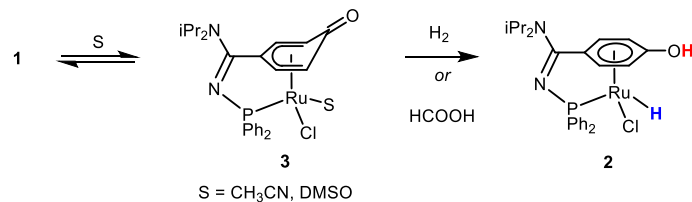


Figure 5 Cycles of hydrogen storage (charge) and release (discharge) with **1**

Finally, the latent behaviour of the catalyst in a full storage and release cycle was investigated. For this purpose, a reactor was loaded with 10 mg ($9.2 \cdot 10^{-3}$ mmol) of **1** in DMSO and then pressurised with 30 bar of CO₂ and 30 bar of H₂. After 20 h at 60 °C, the reactor was allowed to cool down to room temperature and the pressure gently released. The reactor was then closed and stored at room temperature over a week-end (c.a. 65 h). After this storage period, no significant pressure developed in the reactor (not detectable on the pressure gauge). However, 25 mL of gas were released at room temperature over a period of 5 minutes after which the gas flow dropped to 0. The reactor was then heated at 90 °C resulting in the immediate release of gas. This gas evolution stopped after 1 h, with a total volume released of 104 mL, demonstrating that the catalytic species

or its resting state has a certain degree of latency and very high stability. This catalyst latency could prove very useful from a practical and economic point of view and pave the way for an original and sustainable energy delivery concept. Following hydrogenation of CO₂ under moderate pressure, the reactor can be safely transported as is, from the hydrogenation plant to the hydrogen delivery site where formic acid dehydrogenation will be implemented. Another interest inherent to formic acid dehydrogenation is that the hydrogen acceptor (CO₂) is released in high purity hence allowing for low cost capture and storage. This CO₂ can further be used in local or nearby industrial processes rather than being returned to the hydrogenation site. This is a major difference and advantage *vs* other type of LOHCs such as polyaromatics that will necessarily need to be shipped back to the hydrogenation site for hydrogen reloading. However, this very appealing energy delivery concept will need to be improved to be viable, with the efficiency, stability and cost being of prime importance. This concept could also be envisioned with methanol which carries more hydrogen than formic acid (99 g.L⁻¹ *vs* 53 g.L⁻¹). However, the direct hydrogenation of CO₂ into MeOH and the reverse selective dehydrogenation of methanol are not yet straightforward processes.^{35,36}

A thorough study of the reactivity of **1** under various reaction condition was previously reported. In particular, these studies revealed that the ruthenium-hydride **2** could be obtained from **1** and H₂ through intermediate **3** in acetonitrile or directly from **1** in dichloromethane.¹⁷ It is noteworthy that compounds **2** and **3** feature a structure and reactivity very similar to that of the Shvo catalyst (Scheme 1), hence, we believe that those complexes could play a key role in the hydrogenation of CO₂ and dehydrogenation of formic acid. The reactivity of **1** in DMSO with formic acid was studied to highlight potential intermediates. Unfortunately, several ruthenium hydride species were observed of which one was found very stable but our efforts to isolate and characterize this compound were not successful (see SI for full details of this study).



Scheme 1 Hypothetical species involved in hydrogen storage and release processes with the dimeric pre-catalyst **1**.

Conclusion

In conclusion, we have demonstrated the activity of the dimeric tethered complex **1** in the base-free hydrogenation of CO₂ and dehydrogenation of formic acid. An unprecedented base-free hydrogen storage and release cycle has been completed, in which 94% of the hydrogen initially stored was released. This procedure could be repeated over 4 cycles albeit with an observed erosion of the performance which should not minimize the remarkable stability of the catalyst that was still active after 3 hydrogen storage (30 bar CO₂ + 30 bar H₂, 60 °C, 20 h) and release (90 °C; 90-120 min) cycles representing in total, 6 unitary catalytic reactions. We have also demonstrated that this catalyst displays some latency that allows the preparation of ready-to-use formic acid and catalyst solutions. This latent behaviour was further extended to the demonstration of an environmentally sustainable concept enabling the straightforward storage and release of hydrogen. This later original concept would drastically facilitate the process of hydrogen transportation and delivery. These first results with this type of catalyst are truly promising and the design of catalysts of this family are under active studies to improve their performances. In particular, the nature of the tethered arm is being investigated. Further work is ongoing in this direction as well as mechanism studies through experimental and theoretical investigations.

Supporting Information.

Experimental details for CO₂ hydrogenation and formic acid dehydrogenation; CO detection ; latency studies; NMR monitoring of **1** with FA.

AUTHOR INFORMATION

Corresponding Author

Cédric Fischmeister, Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, 35042 Rennes, France. E-mail : cedric.fischmeister@cnrs.fr. <https://orcid.org/0000-0002-9490-8145>

Alain Igau, CNRS, Laboratoire de Chimie de Coordination – UPR 8241. 205, route de Narbonne. BP 44099. 31077 Toulouse cedex 4. alain.igau@lcc-toulouse.fr. <https://orcid.org/0000-0002-5944-1527>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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