Chemistry
A European
Journal

Chemistry
Europe
European Chemical
Societies Publishing

Accepted Article

Title: A Reversible Liquid to Liquid Organic Hydrogen Carrier System Based on Ethylene Glycol and Ethanol

Authors: Quan-Quan Zhou, You Quan Zou, Yehoshoa Ben David, and David Milstein

To be cited as: *Chem. Eur. J.* 10.1002/chem.202002749

Link to VoR: https://doi.org/10.1002/chem.202002749

WILEY-VCH

A Reversible Liquid to Liquid Organic Hydrogen Carrier System Based on Ethylene Glycol and Ethanol

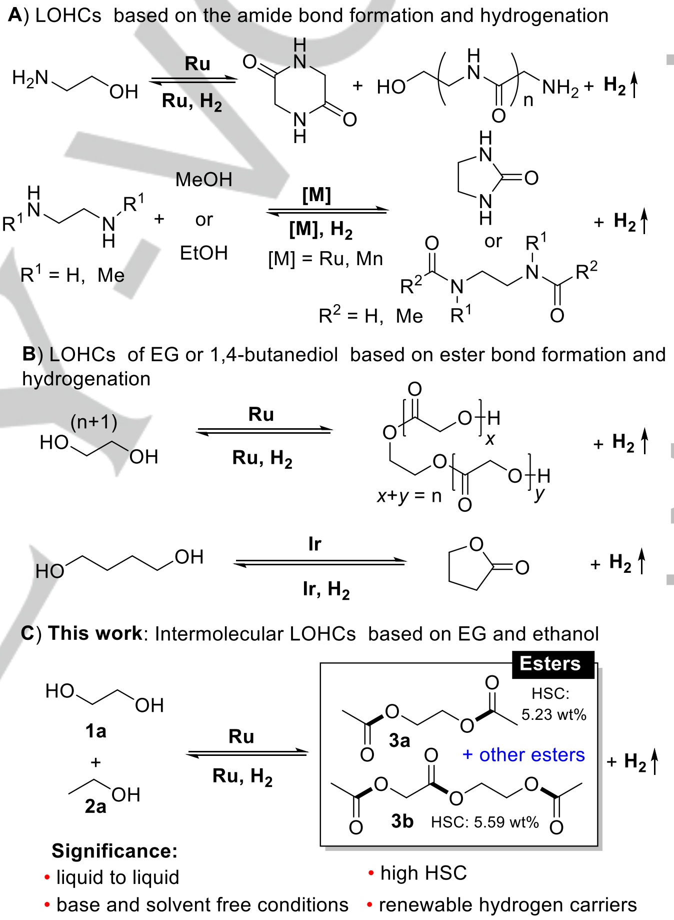
Quan-Quan Zhou,[†] *You-Quan Zou,*[†] *Yehoshoa Ben-David and David Milstein*[*]

Abstract: Liquid organic hydrogen carriers (LOHCs) are powerful systems for the efficient unloading and loading molecular hydrogen. Herein, a liquid to liquid organic hydrogen carrier system based on reversible dehydrogenative coupling of ethylene glycol (EG) with ethanol catalysed by ruthenium pincer complexes is reported. Noticeable advantages of the current LOHC system is that both reactants (hydrogen-rich components) and the produced esters (hydrogen-lean components) are liquids at room temperature, and the dehydrogenation process can be performed under solvent and base-free conditions. Moreover, the hydrogenation reaction proceeds under low hydrogen pressure (5 bar), and the LOHC system has a relatively high theoretical gravimetric hydrogen storage capacity (HSC >5), presenting an attractive hydrogen storage system.

Molecular hydrogen is regarded as the cleanest and most efficient energy carrier because of its high gravimetric energy density and the generation of water as the sole product upon combustion,[1] and much research has been paid towards its utilization as an energy carrier, the so-called "hydrogen economy".[2] However, the safe and efficient storage of hydrogen is still a major challenge, due to the low volumetric energy density and the broad explosion limits of hydrogen gas.[3] Thus, developing new methods for the convenient storage and transportation of hydrogen are highly desirable.

Over the past decades, a variety of hydrogen storage protocols such as compression in pressurized or cryogenic tanks, storage in metal hydrides or absorption in metal organic frameworks have been established.[4] Recent developments indicate that liquid organic hydrogen carriers (LOHC) represent an attractive and safe alternative because of their economic, technical, and environmental advantages in storing and transporting hydrogen.[5] In general, LOHCs are capable of unloading and loading hydrogen by catalytic dehydrogenation of hydrogen-rich liquids and hydrogenation of the resulting hydrogen-lean liquids. Earlier studies on the application of LOHCs are mainly focused on the interconversion between dehydrogenation of cyclic hydrocarbons and the reverse hydrogenation of the resulting aromatic compounds such as methylcyclohehane/toluene[6], perhydrodibenzyltoluene/ dibenzyltoluene[7] systems and so on. Their high hydrogen storage capacities (HSC) and low cost make these systems attractive. Nevertheless, in light of the relatively high bond dissociation enthalpy of non-activated C-H bonds and the strong endothermicity of the dehydrogenation reaction, harsh conditions are always required (reaction temperature above 250 °C), resulting in high energy consumption and degradation.[6],[8]

Dehydrogenation of N- heterocycles is more favourable and LOHCs based on them have received much attention,[9] but there are still some limitations of most reported systems, such as soild dehydrogenated products, use of solvents, and usually high hydrogen pressure (> 50 bar of H_2) for the reverse hydrogenation process. Therefore, there is still much interest in finding new and efficient liquid to liquid hydrogen carriers.



Scheme 1. LOHCs based on catalytic alcohol dehydrogenative coupling and hydrogenation reactions.

In recent years, homogeneous acceptorless dehydrogenative coupling reactions catalysed by pincer complexes have resulted in atom-economic and green synthetic organic chemistry, the sole by-product being hydrogen gas.[10] In this context, we have developed the acceptorless dehydrogenative amidation and esterification using alcohols and amines catalysed by metal pincer complexes, which enable the synthesis of a series of amides and esters in a green and sustainable manner. Moreover, the formed amides and esters products could be readily hydrogenated back to the corresponding alcohols and amines.[11] These (de)hydrogenation reactions allowed us to develop

---

[*] Q.-Q. Zhou, Y.-Q. Zou, Y. Ben-David, Prof. D. Milstein
Department of Organic Chemistry, Weizmann Institute of Science, Rehovot 76100, (Israel)
E-mail: david.milstein@weizmann.ac.il

[†] Q.-Q. Zhou and Y.-Q. Zou contributed equally to this work.

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) several LOHC systems. In 2015, our group firstly established a LOHC system based on the dehydrogenative coupling of 2-aminoethanol to the cyclic dipeptide diketoperazine and its reverse hydrogenation using a ruthenium pincer catalyst (Scheme 1A).[12] Recently, two efficient LOHC systems based on ethylenediamine/methanol and ethyleneamine/ethanol were independently reported by our group and the Prakash group based on the catalytic amidation and reversible hydrogenation reactions catalyzed by ruthenium pincer complexes (Scheme 1A).[13] Very recently, an LOHC system based on dimethylethylenediamine/methanol catalyzed by a manganese pincer complex was reported by the Liu group (Scheme 1A).[13] Although potentially useful, the products of these amidation reactions are solids at room temperature, and a solvent is used, diminishing the HSC. Moreover, the reverse hydrogenation of amides requires high pressure of H_2 (50-70 bar). Consequently, developing a liquid to liquid organic hydrogen carrier system using inexpensive organic liquids with high HSC is still a challenging task.

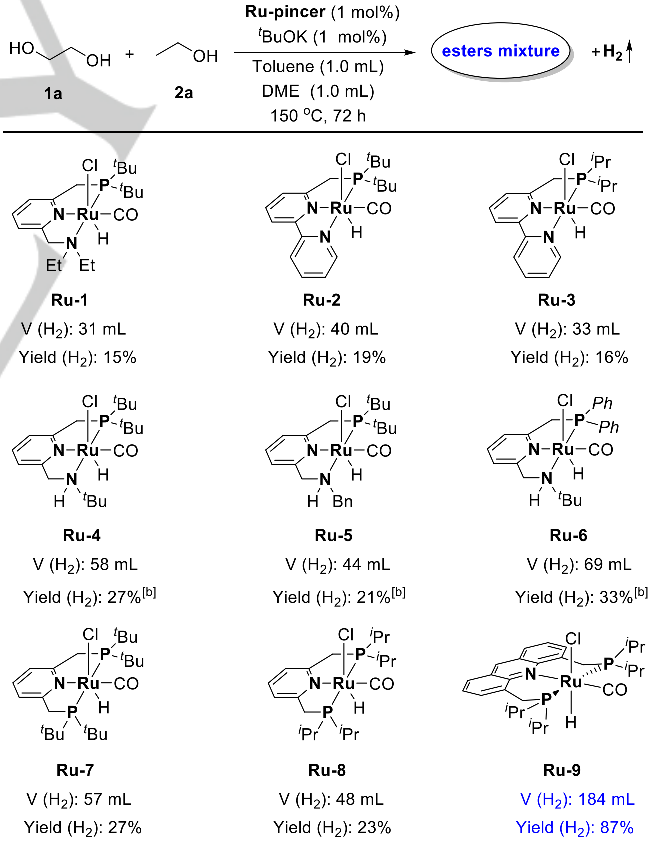
LOHC systems using alcohols based on dehydrogenative coupling of alcohols to form esters and the reverse hydrogenation are rarely reported.[14] Ethylene glycol (EG), the simplest and abundant vicinal diol, has a high potential gravimetric HSC, and can be considered as an inexpensive and efficient hydrogen carrier.[15] Our group has recently developed an effective LOHC system based on ethylene glycol. Using a ruthenium pincer complex as the catalyst, ethylene glycol could be converted to oligoesters accompanied with the generation H_2 through dehydrogenative esterification. The reverse hydrogenation was accomplished with the same catalyst (Scheme 1B).[16] Fujita et al. developed a LOHC system based on iridium catalyzed dehydrogenative lactonization of 1,4-butanediol and the reverse hydrogenation (Scheme 1B).[14b] Beller and co-workers developed an efficient dehydrogenative coupling process of ethanol catalyzed by a ruthenium pincer complex, for the production of ethyl acetate. [17]

From economic and environmental points of view, the development of novel LOHCs using simple, readily available in bulk quantities, renewable and cheap alcohols would expand the utility of acceptorless dehydrogenation strategy in hydrogen storage.[18] To the best of our knowledge, the intermolecular acceptorless dehydrogenative coupling of EG with ethanol (or any other alcohol) has never been reported. Herein, we report a LOHC system based on ruthenium pincer catalyzed dehydrogenative coupling of EG with ethanol and the reverse hydrogenation reaction of the mixed ester products (Scheme 1C); the theoretical HSC based on EG-ethanol / ethane-1, 2-diyl diacetate (**3a**) is 5.23 wt%, and based on EG-ethanol / 2-acetoxyethyl 2-acetoxyacetate (**3b**) is 5.59 wt%, both exceeding the EU target (5.0 wt%).[19]

We started the investigation with the dehydrogenative coupling of EG **1a** (2.0 mmol) with ethanol **2a** (4.8 mmol) using ruthenium pincer catalysts developed in our group[13a, 20] (Table 1). Initially, this reaction was conducted in the presence of 1 mol% of the pincer complex **Ru-1** and 1 mol% of potassium tert-butoxide (^{t}BuOK, required for deprotonation of **Ru-1** to form the active dearomatized form) in a solvent mixture of toluene (1 mL) and ethylene glycol dimethyl ether (DME, 1 mL) at 150 °C (bath temperature) for 72 h. As a result, 31 mL of hydrogen gas were collected, representing 15% yield (yield is defined with respect to full conversion of EG (2.0 mmol) to ethane-1,2-diyl diacetate **3a** and the excess ethanol (0.8 mmol) conversion to ethyl acetate). The ruthenium (PNN) complexes **Ru-2** and **Ru-3** also catalysed the reaction under the same conditions producing hydrogen gas in 19% and 16% yields, respectively. Using the (PNNH) complexes **Ru-4** to **Ru-6** as pre-catalysts, the yield of H_2 gas was improved to 33%, and similar yields were obtained using the (PNP) complexes **Ru-7** and **Ru-8**. Remarkably, using the acridine-based PNP ruthenium complex **Ru-9** under the same conditions, a significant increase in the catalytic activity was observed, yielding 184 mL (7.7 mmol, 87% yield) of H_2 with >99.85% purity (see SI for more details).

With the optimal conditions in hand using **Ru-9**, we next examined the identity of the produced esters. In theory, the dehydrogenative coupling of EG and ethanol could generate a mixture of nine esters. We analyzed the ester mixture and isolated the esters by flash chromatography. Ethane-1, 2-diyl diacetate **3a** was detected as one of the main products (18.5% yield), and ethyl acetate was obtained in 13% GC yield (0.31 mmol). Moreover, ethyl 2-hydroxyacetate, 2-acetoxyethyl 2-acetoxyacetate, 2-acetoxyethyl 2-hydroxyacetate, and 2-hydroxyethyl acetate were detected and isolated (see SI for more details).

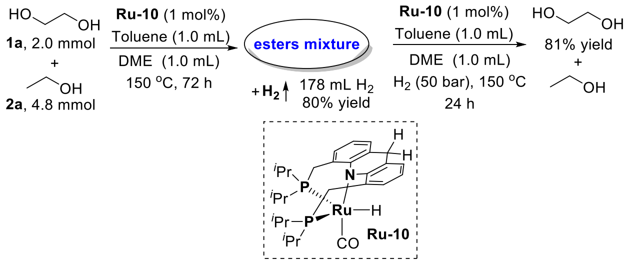
Table 1: Results for dehydrogenative coupling of EG with ethanol catalysed by ruthenium pincer complexes.[a]



[a] Reaction conditions: **1a** (2.0 mmol), **2a** (4.8 mmol), Ru-pincer (0.02 mmol, 1 mol%), ^{t}BuOK (1 mol%), toluene (1.0 mL), DME (1.0 mL), in 100 mL Young-type Schlenk tube, 150 °C (oil bath temperature), 72 h; yield of H_2 was calculated on the basis of H_2 volume (192 mL for 2 mmol EG and 4 mmol ethanol with respect to 100% yield of ethylene glycol diacetate **3a**, and 19.2 mL for the 0.8 mmol excess ethanol with respect to 100% yield of ethyl acetate);

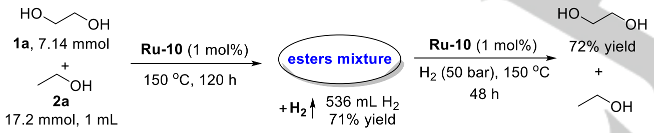
the volume of hydrogen was measured every 24 hours. [b] 2 mol% ${}^tBuOK$ was used.

Encouraged by the results of acridine-based PNP ruthenium complex **Ru-9**, we tested the catalytic performance of the stable dearomatized acridine PNP ruthenium complex **Ru-10**. Significantly, the dehydrogenative coupling reaction worked quite well under base-free conditions, and 80% yield of hydrogen gas was recorded, and the ester mixture could be fully hydrogenated back to EG and ethanol using the same catalyst under 50 bar of H_2 with a 81% NMR yield of EG (Scheme 2).



Scheme 2. Dehydrogenative coupling of EG and ethanol and the reverse hydrogenation under base-free conditions.

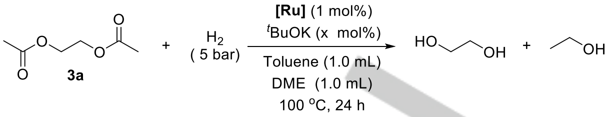
Avoiding the use of solvents in the dehydrogenation process of LOHC systems is desirable, regarding the HSC of the system. With this in mind, we tested **Ru-10** as a catalyst for the dehydrogenative esterification of EG and ethanol under solvent- and base-free conditions using a larger scale. Gratifyingly, 536 mL of H_2 gas (22.3 mmol, 71% yield) were collected using 1 mL ethanol (17.2 mmol) and 7.14 mmol EG. Significantly, the resulting ester mixture could be fully hydrogenated back to EG and ethanol with a 72% yield using the same catalyst **Ru-10** under 50 bar of H_2 and solvent- and base-free conditions (Scheme 3).



Scheme 3. Large-scale dehydrogenative coupling of EG and ethanol and the reverse hydrogenation catalysed by the dearomatized **Ru-10** under solvent- and base-free conditions.

Following the successful demonstration of the dehydrogenative coupling of EG and ethanol in the unloading of hydrogen and the reverse hydrogenation process, we evaluated the potential of our pincer catalysts in catalyzing the hydrogenation process under lower pressure. We previously reported ruthenium pincer catalysts capable of hydrogenation of esters under low pressure.[20] Guided by this, we examined the hydrogenation of **3a** with our pincer complexes using 5 bar pressure of H_2. As shown in Table 2, the ruthenium catalysts **Ru-10**, **Ru-1** and **Ru-5** were screened using a mixture of toluene and DME as solvent. The best hydrogenation catalyst was **Ru-5** which catalysed the hydrogenation of ester **3a** under 5 bar with 99% yield.

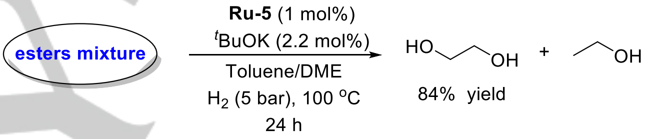
Table 2: Hydrogenation of ester **3a**.[a]



Entry	[Ru]	${}^tBuOK$ (mol %)	Yield [%][b]
1	**Ru-10**	-	55
2	**Ru-1**	2.2	71
3	**Ru-5**	2.2	99

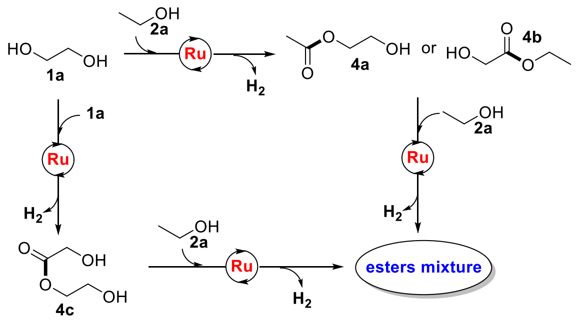
[a] Reaction conditions: **3a** (1.0 mmol), Ru-pincer complex (0.01 mmol, 1 mol%), ${}^tBuOK$ (0-2.2 mol%), H_2 (5 bar), toluene (1.0 mL), DME (1.0 mL), in Fisher-Porter tubes, 100 °C (oil bath temperature), 24 h. [b] Yields of EG were determined by ${}^1H$ NMR with mesitylene as internal standard.

We next examined the hydrogenation of the ester mixture formed by dehydrogenative coupling of EG and ethanol, in toluene/DME as described above in Table 1(**Ru-9** as catalyst). The reaction was performed in the presence of 1 mol% **Ru-5**, 2.2 mol% ${}^tBuOK$, and 5 bar of hydrogen gas at 100 °C for 24 h (Scheme 4). Gratifyingly, the ester mixture was fully hydrogenated back to EG and ethanol with a 84% NMR yield of EG (the yield of ethanol was determined as 72%, the losses attributed to its volatility).



Scheme 4. Reversible hydrogenation of the reaction mixture.

According to our previous investigations on dehydrogenative coupling reactions,[11a],[16] we propose a possible overall catalytic pathway for the dehydrogenative coupling of EG and ethanol. As shown in Scheme 5, one equivalent of EG initially reacts with ethanol to generate 2-hydroxyethyl acetate (**4a**) or ethyl 2-hydroxyacetate (**4b**) with the release of two equivalents of hydrogen gas. Simultaneously, EG can also couple with another molecule of EG to generate 2-hydroxyethyl 2-hydroxyacetate (**4c**) along with the generation of 2 equivalents H_2. Subsequently, **4a**, **4b,** and **4c** can react with excess ethanol through similar processes to produce the final ester products, releasing H_2.



Scheme 5. Proposed pathway for the dehydrogenative coupling of EG with ethanol.

In conclusion, we have developed a new efficient liquid to liquid organic hydrogen carrier system by ruthenium pincer catalyzed dehydrogenative esterification of EG and ethanol and the reverse hydrogenation under low pressure. Both the reactants EG and ethanol are abundant, cheap, sustainable and relatively non-toxic industrial raw materials. Moreover, the dehydrogenative esterification can be conducted under solvent- and base-free conditions, thus offering, upon further development, a promising approach for application in hydrogen storage and portable energy systems.

Acknowledgements

D. M. holds the Israel Matz Professorial Chair of Organic Chemistry. Y.-Q. Z. acknowledges the Sustainability and Energy Research Initiative (SAERI) of Weizmann Institute of Science for a research fellowship.

Conflict of interest

The authors declare no conflict of interest.

Keywords: hydrogen carrier • ethylene glycol • ethanol • dehydrogenation • ruthenium pincer

[1] a) R. Cammack, M. Frey, R. Robson, *Hydrogen as a Fuel: Learning from Nature;* Taylor & Francis: London, **2002**; b) A. Midilli, M. Ay, I. Dincer, M. A. Rosen, *Renewable Sustainable Energy Rev.* **2005**, *9*, 255; c) M. Balat, *Int. J. Hydrogen Energy* **2008**, *33*, 4013; d) J. O'. M. Bockris, *Int. J. Hydrogen Energy* **2013**, *38*, 2579; e) S. Singh, S. Jain, A. K. Tiwari, M. R. Nouni, J. K. Pandey, S. Goel, *Renewable Sustainable Energy Rev.* **2015**, *51*, 623.

[2] a) J. O'.M. Bockris, *Science* **1972**, *176*, 1323; b) L. Schlapbach, A. Zuttel, *Nature* **2001**, *414*, 353; c) T. Valdés-Solís, *Int. J. Hydrogen Energy* **2007**, *32*, 1625.

[3] a) S. Satyapal, J. Petrovic, C. Read, G. Thomas, G. Ordaz, *Catal. Today* **2007**, *120*, 246; b) A. Léon, *Hydrogen technology, in Mobile and Portable Applications*, Springer-Verlag, Berlin, Heidelberg, **2008**; c) U. Eberle, M. Felderhoff, F. Schüth, *Angew. Chem., Int. Ed.* **2009**, *48*, 6608; *Angew. Chem.* **2009**, *121*, 6732; d) L. J. Murray, M. Dincâ, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294; e) D. Minic, (ed.) *Hydrogen Energy—Challenges and Perspectives*; InTech, **2012**; f) A. F. Dalebrook, W. Gan, M. Grasemann, S. Moret, G. Laurenczy, *Chem. Commun*. **2013**, *49*, 8735; g) T. He, P. Pachfule, H. Wu, Q. Xu, P. Chen, *Nat. Rev. Mater.* **2016**, 16059.

[4] a) J. Graetz, *Chem. Soc. Rev.* **2009**, *38*, 73; b) Z. Huang, T. Autrey, *Energy Environ. Sci.* **2012**, *5*, 9257; c) M. P. Suh, H. J. Park, T. K. Prasad, D.-W. Lim, *Chem. Rev.* **2012**, *112*, 782; d) S.-L. Li, Q. Xu, *Energy Environ. Sci.* **2013**, *6*, 1656; e) S. Dutta, *J. Ind. Eng. Chem.* **2014**, *20*, 1148.

[5] a) R. H. Crabtree, *Energy Environ. Sci.* **2008**, *1*, 134; b) P. Makowsky, A. Thomas, P. Kuhn, F. Goetmann, *Energy Environ. Sci.* **2009**, *2*, 480; c) T. He, Q. Pei, P. Chen, *J. Energy Chem*. **2015**, *24*, 587; d) P. Preuster, C. Papp, P. Wasserscheid, *Acc. Chem. Res.* **2017**, *50*, 74; e) E. Gianotti, M. Taillades-Jacquin, J. Rozière, D. J. Jones, *ACS Catal.* **2018**, *8*, 4660; f) T. Shimbayashi, K. Fujita, *Tetrahedron* **2020**, *76*, 130946.

[6] a) M. Taube, D. W. T. Rippin, D. L. Cresswell, W. Knecht, *Int. J. Hydrogen Energy* **1983**, *8*, 213; b) T. Schildhauer, E. Newson, S. Muller, *J. Catal.* **2001**, *198*, 355; c) S. Yolcular, O. Olgun, *Catal. Today* **2008**, *138*, 198.

[7] a) N. Brückner, K. Obesser, A. Bösmann, D. Teichmann, W. Arlt, J. Dungs, P. Wasserscheid, *ChemSusChem* **2014**, *7*, 229; b) K. Müller, K. Stark, V. N. Emel'yanenko, M. A. Varfolomeev, D. H. Zaitsau, E. Shoifet, C. Schick, S. P. Verevkin, W. Arlt, *Ind. Eng. Chem. Res.* **2015**, *54*, 7967.

[8] a) N. Kariya, A. Fukuoka, M. Ichikawa, *Appl. Catal. A* **2002**, *233*, 91; b) S. Hodoshima, S. Takaiwa, A. Shono, K. Satoh, Y. Saito, *Appl. Catal. A* **2005**, *283*, 235; c) E. Clot, O. Eisenstein, R. H. Crabtree, *Chem. Commun.* **2007**, 2231; d) R. B. Biniwale, S. Rayalu, S. Devotta, M. Ichikawa, *Int. J. Hydrogen Energy* **2008**, *33*, 360.

[9] a) Y. Cui, S. Kwok, A. Bucholtz, B. Davis, R. A. Whitney, P. G. Jessop, *New J. Chem.* **2008**, *32*, 1027; b) Fujita, Y. Tanaka, M. Kobayashi, R. Yamaguchi, *J. Am. Chem. Soc.* **2014**, *136*, 4829.

[10] a) C. Gunanathan, D. Milstein, *Science* **2013** *341*, 1229712; b) J. R. Khusnutdinova, D. Milstein, *Angew. Chem., Int. Ed.* **2015**, *54*, 12236; *Angew. Chem.* **2015**, *127*, 12406; c) A. Kumar, T. M. Bhatti, A. S. Goldman, *Chem. Rev.* **2017**, *117*, 12357; d) H. Valdés, M. A. García-Eleno, D. Canseco-Gonzalez, D. Morales-Morales, *ChemCatChem* **2018**, *10*, 3136.

[11] a) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*,10840; b) C. Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, *317*, 790; c) D. Srimani, E. Balaraman, B. Gnanaprakasam, Y. Ben-David, D. Milstein, *Adv. Synth. Catal.* **2012**, *354*, 2403; d) D. Srimani, E. Balaraman, P. Hu, Y. Ben-David, D. Milstein, *Adv. Synth. Catal.* **2013**, *355*, 2525.

[12] P. Hu, E. Fogler, Y. Diskin-Posner, M. A. Iron, D. Milstein, *Nat. Commun.* **2015**, *6*, 6859.

[13] a) P. Hu, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2016**, *55*, 1061; *Angew. Chem.* **2016**, *128*, 1073; b) J. Kothandaraman, S. Kar, R. Sen, A. Goeppert, G. A. Olah, G. K. S. Prakash, *J. Am. Chem. Soc.* **2017**, *139*, 2549; c) Y. Xie, P. Hu, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2019**, *58*, 5105; *Angew. Chem.* **2019**, *131*, 5159; d) Z.-H. Shao, Y. Li, C, Liu, W. Ai, S.-P. Luo, Q. Liu, *Nat. Commun.* **2020**, *11*, 591.

[14] a) P. J., Jr. Bonitatibus, S. Chakraborty, M. D. Doherty, O. Siclovan, W. D. Jones, G. L. Soloveichik, *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112*, 1687; b) M. Onoda, Y. Nagano, K. Fujita, *Int. J. Hydrogen Energy* **2019**, *44*, 28514.

[15] H. Yue, Y. Zhao, X. Ma, J. Gong, *Chem. Soc. Rev.* **2012**, *41*, 4218.

[16] Y.-Q. Zou, N. von Wolff, A. Anaby, Y. Xie, D. Milstein, *Nat. Catal.* **2019**, *2*, 415.

[17] M. Nielsen, H. Junge, A. Kammer, M. Beller, *Angew. Chem. Int. Ed.* **2012**, *51*, 5711; *Angew. Chem.* **2012**, *124*, 5809.

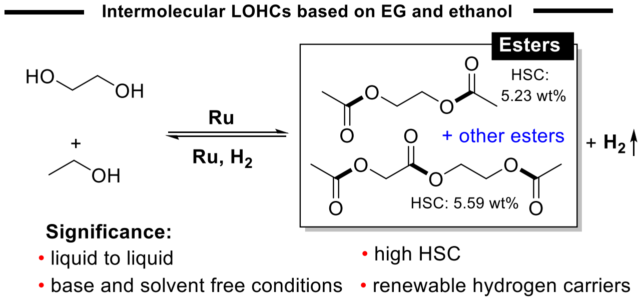
[18] a) J. Goldemberg, *Science* **2007**, *315*, 808; b) M. Iwamoto, K. Kasai, T. Haishi, *ChemSusChem* **2011**, *4*, 1055.

[19] Fuell Cells and Hydrogen Joint Undertaking (FCH2 JU) Governing Board. Multi-Annual Work Plan 2014-2020; FCH2 JU: Brussels, Belgium, **2014**.

[20] a) C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588; b) E. Fogler, J. A. Garg, P. Hu, G. Leitus, L. J. W. Shimon, D. Milstein, *Chem. Eur. J.* **2014**, *20*, 15727.

Entry for the Table of Contents

COMMUNICATION



A liquid to liquid organic hydrogen carrier system based on reversible dehydrogenation and hydrogenation reactions using ethylene glycol and ethanol is reported. Both the reactants are abundant, cheap and non-toxic industrial raw materials. Moreover, this dehydrogenative esterification as well as hydrogenation can be conducted under base- and solvent- free conditions, thus offering a promising approach for application in hydrogen storage.

*Quan-Quan Zhou, You-Quan Zou, Yehoshoa Ben-David and David Milstein**

Page No. – Page No.

A Reversible Liquid to Liquid Organic Hydrogen Carrier System Based on Ethylene Glycol and Ethanol