



Review

Hydrogen activation on organometallic complexes and H₂ production, utilization, and storage for future energy

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ABSTRACT

This perspective article serves to highlight the contributions to this special volume of Journal of Organometallic Chemistry entitled "Organometallics for Energy Conversion". The key features of dihydrogen coordination to transition metal complexes are discussed in the context of the challenge of producing and utilizing hydrogen as the energy carrier of the future. Ultimately, production of H₂ fuel from water will be needed rather than its current production principally from natural gas. Schemes involving use of solar energy to split water are currently of high interest, and a massive research effort is underway worldwide to accomplish this goal. This is primarily a *chemistry* problem (rather than engineering or materials), and it can then be assumed that organometallic chemistry will play an important role for both hydrogen production and storage.

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Contents

1. Introduction	2648
1.1. Dihydrogen coordination and splitting	2649
1.2. New materials for hydrogen storage	2650
2. Biomimetic H ₂ production, photocatalytic water splitting, and fuel cells	2651
References	2652

1. Introduction

As eminently expressed by Lewis and Nocera [1], "the supply of secure, clean and sustainable energy is arguably the most important scientific and technical challenge facing humanity in the 21st century". These prominent researchers in the field go on to say "meeting global energy demand in a sustainable fashion will require not only increased energy efficiency and new methods of using existing carbon-based fuels but also a daunting amount of new carbon-neutral energy." Nocera has often stated that this is primarily a *chemistry* problem (rather than engineering or materials), and it can then be assumed that organometallic chemistry will play an important role. Hydrogen is of course the ideal energy carrier, but vexing challenges exist. Ultimately, production of H₂ fuel from water will be needed rather than its current production principally from natural gas. Schemes involving use of solar energy to split water are currently of high interest [1], and determining pre-

cisely how plants use cheap and abundant metals to accomplish this would be a monumental achievement [2]. Current man-made water splitting catalysts rely on precious metals that would not be abundant enough to fulfill future world energy demand. Furthermore it must be kept in mind that vast quantities of hydrogen are also vital in chemical processes: catalytic hydrogenations are the largest-volume human-made chemical reactions in the world. All crude oil is treated with H₂ to remove sulfur and nitrogen, and hundreds of million tons of ammonia fertilizer are produced annually from H₂ and N₂ by the Haber process that supports much of the world's population.

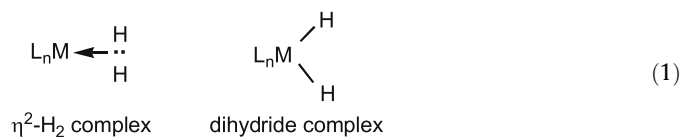
In addition to production, a major challenge exists to develop lightweight materials for H₂ storage for vehicle use. *Reversible* schemes are key: although H₂ can readily be extruded from a variety of compounds, it can be difficult to re-add. The materials also must be light and contain >6% by weight H₂, reducing prospects for known facile reversible systems such as metal–H₂ or hydride complexes. The ideal binding energy for reversible H₂ absorption to materials is of the order of 3–5 kcal/mol, but such binding currently can only be achieved at low temperature, e.g. liquid nitrogen

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temperature, at moderate pressures of H₂ (several atmospheres). This perspective article will discuss the activation of hydrogen underlying both hydrogen production and storage. Coordination and splitting of H₂ is now known to occur not only on transition metal centers but also on main group compounds, a promising new finding which can even lead to catalytic hydrogenation reactions. Catalysis may involve H₂ complexes at least as intermediates, and H₂ complexes have been implicated in solar energy conversion schemes based on photodissociation of water [3]. Non-metal based hydrogen storage and catalysis of H₂ reactions would be beneficial because of the lighter weight and potentially lower cost of main group materials.

To obtain proper perspective, one needs to be aware of how activation (the bond cleavage process) of H₂ occurs on metal complexes (e.g. industrial catalysts) and on enzymes in nature such as hydrogenases. The H₂ molecule is held together by a very strong two-electron H–H bond and is only useful chemically when the two H's are split apart in a controlled fashion. Remarkably, the detailed mechanism at the molecular level by which the H–H bond splits to form for example a metal dihydride complex was not clearly established until only relatively recently in the history of H₂ activation. One of the reasons is that H₂ had not been found to chemically bind to a metal center, usually the first step in breaking up a strong bond, until the discovery by Kubas and coworkers in 1984 [4]. The coordination of a nearly intact H₂ molecule to the organometallic complexes, M(CO)₃(PR₃)₂(H₂) (M = Mo, W), led to a new paradigm in chemistry. The H₂ binds side-on (η^2) to the metal center primarily via donation of its two σ electrons to a vacant d orbital to form a *stable* dihydrogen complex rather than being oxidatively added to form a dihydride.



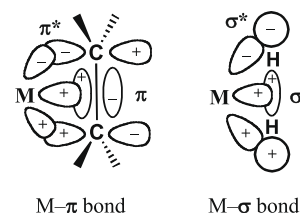
Furthermore, it was eventually found that virtually any σ bond (C–H, Si–H, B–H, etc.) can bind to a metal center to form a “ σ complex” [5] that is crucial to activation of hydrogen containing molecules. For example, B–H bond coordination of boron compounds to metals is relevant to catalytic hydrogen storage schemes using low molecular weight boranes. This special volume will present a number of papers where H–H and other sigma bond activations [4b,5] on organometallic complexes are important to both energy conversion and storage methodologies.

1.1. Dihydrogen coordination and splitting

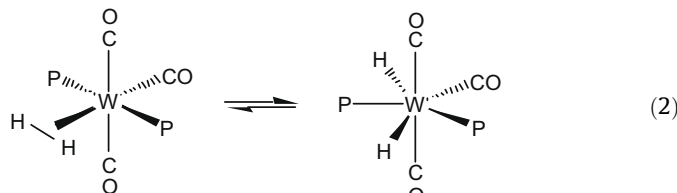
Dihydrogen coordination was first demonstrated in the complex W(CO)₃(PⁱPr₃)₂(H₂) [4]. The H–H bond length (0.89 Å) is lengthened ~20% over that in H₂ (0.74 Å), showing that H₂ is not physisorbed but rather chemisorbed, with the bond “activated” towards rupture. A compelling diagnostic for the degree of activation is observation of the HD one-bond coupling constant in the proton NMR of the HD isotopomer. For example $J_{\text{HD}} = 33.5$ Hz for W(CO)₃(PⁱPr₃)₂(HD) vs. 43.2 Hz in HD gas, indicating that the H–D bond is mostly intact. Observation of J_{HD} higher than that for a dihydride complex (>2 Hz) is the premier criterion for an H₂ complex. Many new examples of H₂ complexes were soon found by dozens of research groups worldwide [4b,5,6]. The variety and abundance of complexes is remarkable: about 500 H₂ complexes are known (most are stable) for nearly every transition metal and type of co-ligand. They are the focus of over 1500 publications, dozens of reviews, and several monographs. The most frequently asked question after the discovery of H₂ complexes concerned whether they are relevant in catalysis, i.e. can direct transfer of hydrogen from an H₂ ligand to a substrate

occur? This has now been demonstrated in several systems, particularly in Noyori's asymmetric catalytic hydrogenation systems [7] and elegantly employed by nature in hydrogenase enzymes [8]. Despite their apparent simplicity, M–H₂ complexes are arguably the most dynamic, complex, and enigmatic chemical topologies known from a structure/bonding/dynamics viewpoint. Only recently has the viewpoint on dihydrogen complexes shifted from their significance in basic science towards more practical aspects, most importantly hydrogen production and storage and the presumed intermediacy of metal–H₂ binding in biological systems such as hydrogenases.

The 3-center metal–H₂ interaction complements classical Werner-type coordination complexes where a ligand donates electron density through its *non-bonding* electron pair(s) and π -complexes in which electrons are donated from π -electrons.

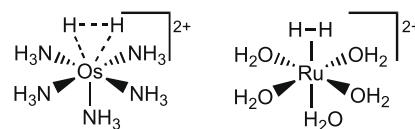


H₂ is thus a weak Lewis base that can bind to strong electrophiles, but transition metals are unique in stabilizing H₂ complexes by *backdonation* of electrons from a filled metal d orbital to the σ^* antibonding orbital of H₂, an interaction unavailable to main group atoms [4b,6,9]. The backdonation is analogous to that for π -complexes, e.g. M–ethylene. Backdonation is crucial not only in stabilizing the bonding but also in splitting the H–H bond. If it is too strong, the H–H bond cleaves to form a dihydride because of overpopulation of the H₂ σ^* orbital. There is often a fine line between H₂ and dihydride coordination, and in some cases *equilibria* exist in solution for W(CO)₃(PR₃)₂(H₂), showing that side-on coordination of H₂ is the first step in H–H cleavage [6]. Theoretical analyses of the bonding and activation of H₂ on metal

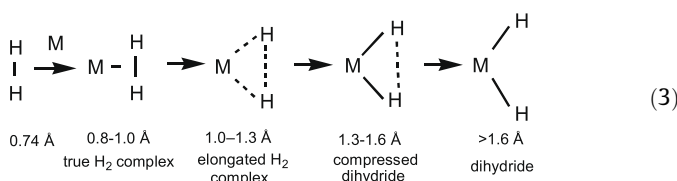


complexes have been extensive and crucial, leading to a synergism between theory and experiment that is unparalleled in chemistry [10]. Several papers in this volume focus on computational modeling of hydrogen splitting.

H₂ complexes are also stable with non-bulky co-ligands such as NH₃ [11,12], in some cases with greatly elongated d_{HH} (1.3 Å for the Os complex [11]).

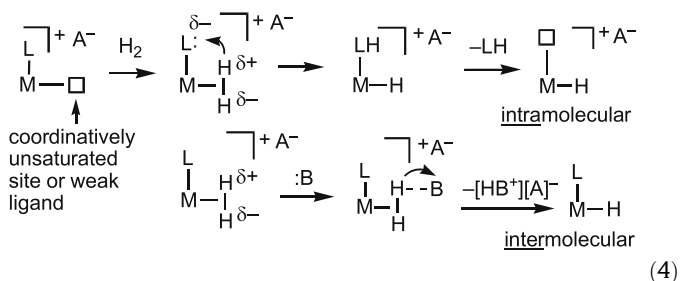


Variation of M, L, and other factors show “arresting” of bond rupture along its entire reaction coordinate where d_{HH} varies enormously from 0.82 to 1.5 Å.

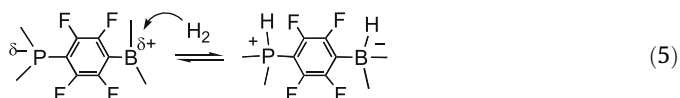


Although the d_{HH} ranges shown in Eq. (3) are arbitrary, each category of complexes has distinct properties. The d_{HH} is relatively short (0.8–1.0 Å) in “true” H_2 complexes best exemplified by $\text{W}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$, much as in physisorbed H_2 where d_{HH} is <0.8 Å. Importantly, even though the binding energy can be as high as 15–20 kcal/mol, the H_2 binding is often completely reversible here, i.e. H_2 can be removed simply upon exposure to vacuum and re-added many times at room temperature. Elongated H_2 complexes and “compressed hydrides” are relative terms since a near continuum of d_{HH} has been observed. First-row M, electron-withdrawing L, and positive charge (cationic complex) favor H_2 binding and shorten d_{HH} . The ligand *trans* to H_2 has a powerful influence: strong π -acceptors such as CO greatly reduce backdonation and normally keep $d_{\text{HH}} < 0.9$ Å.

In addition to homolytic cleavage of H_2 , heterolytic cleavage of bound H_2 can occur [13], a process crucial to both enzymatic (hydrogenase) and non-biological activation of hydrogen that may be key to its future production from water.



The H_2 ligand is deprotonated and the remaining hydrogen ligates to the metal as a hydride. This process can be very facile because the formal oxidation state of M does not change on binding of H_2 , whereas formation of a dihydride formally increases the metal oxidation state by two. H_2 ligands can have far greater thermodynamic and kinetic acidity than most hydride ligands. H_2 gas can be turned into a very strong acid: free H_2 is an extremely weak acid ($pK_a \sim 35$ in THF), but binding it to an electrophilic cationic metal increases the acidity up to 40 orders of magnitude (pK_a can be as low as -6). Heterolysis of H_2 is a crucial step in many industrial and biological processes, including the function of hydrogenase enzymes being modeled for H_2 production, the subject of several papers in this volume. As shown in Eq. (4), H_2 can heterolyze intramolecularly or intermolecularly via protonation of an external base B to give a metal hydride and HB^+ . The latter is the reverse of protonation of a metal hydride that is often used to synthesize H_2 complexes (reactions in Eq. (4) are reversible) [14]. Most significantly, heterolytic splitting has been shown to occur on non-metal systems. Stephan's initial discovery on phosphine-borane species [15] ideally combines both a strongly Lewis acidic center (boron) with a nearby Lewis basic site (phosphorus) that apparently can accept the proton from heterolytic splitting of H_2 (Eq (5)).



Such H_2 activation on “frustrated Lewis acid–base pairs” has now been found in several other systems involving mixtures of sterically encumbered Lewis acids plus nitrogen-based or other types of bases wherein the bulky substituents prevent direct Lewis acid–base interaction [15c]. These systems can even lead to catalytic hydrogenation processes. The metal-free aspect is highly relevant because precious metals such as platinum are most often used in catalysis and can be environmentally unfriendly as well as costly or in short supply. One question is: will we no longer need transition metal or organometallic chemists! I sincerely doubt it (metal *d* or *f* orbitals are invaluable and irreplaceable), but clearly there are now many new avenues for chemical bond splitting and transformations.

1.2. New materials for hydrogen storage

The above discovery of main group splitting of hydrogen is significant because of the reversible nature of the hydrogen activation. Materials for hydrogen storage are a vexing challenge, particularly for vehicles, because they must be lightweight (contain >6% by weight H_2 to be practical). However, energetically favorable extrusion of hydrogen from light non-metal materials is rare (a recent example is H_2 evolution from “hydride-like” organic compounds [16]) and it can be extremely difficult to add hydrogen back. As stated by Jensen in his article in this volume, the utilization of liquid aromatic organic compounds as hydrogen carriers has remained a tantalizing but impractical possibility for over 60 years. His studies of dehydrogenation of *N*-ethyl perhydrocarbazole catalyzed by PCP pincer iridium complexes offer some perspective on this area.

The need for light materials reduces the prospects for known well-established facile reversible systems, e.g. dihydrogen or hydride binding to transition metals. Nonetheless, there has been much recent progress on hydrogen activation by unsaturated mixed-metal cluster complexes that might provide new directions for hydrogen storage and activation and hydrogenation catalysis. This topic of hydrogen-rich polynuclear metal complexes has been reviewed by Adams [17], and an article by Weller in this thematic issue addresses high hydride content rhodium clusters with possible application towards immobilization of redox switchable H_2 binding materials on a surface. At the other end of the spectrum, very low-coordinate iron hydride complexes are reported here by Holland.

Ammonia borane, H_3NBH_3 , is a popular candidate for hydrogen storage and also combines both Lewis acidic (B) and basic (N) centers [18]. Here however these centers are directly bonded, whereas in the “frustrated Lewis acid–base pairs” the acidic and basic sites are separated. Thus catalysis of dehydrogenation of ammonia borane and related boron compounds for chemical hydrogen storage is an important area for research and is addressed both experimentally and computationally in articles in this volume by Repo and Hall. Sabo-Etienne reports σ -bonded borane complexes, possibly an initial step in such activation of ammonia–borane type compounds.

Other popular promising materials for H_2 storage are metal–organic frameworks (MOFs) that have huge surface area capable of binding large numbers of H_2 molecules [19–20]. Excellent recent reviews by Antonelli, Long, and Thomas cover the adsorption and desorption of hydrogen on metal–organic framework materials in comparison with other nanoporous materials [20]. In the MOF materials, inelastic neutron scattering (INS) studies by Eckert are critical in determining whether H_2 binds to unsaturated metal centers in η^2 - H_2 fashion and/or is physisorbed in the framework [19]. Storage of H_2 by physisorption (or weak chemisorption) on solid surfaces is attractive since it provides fast kinetics and low heat effects during adsorption/desorption cycles. Although this topic is not addressed in this volume, the MOF complexes are often highly metal–organic in nature, albeit without actual M–C bonding. For example MOF polymers of composition $[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_2]$ (L = tetracarboxylate ligands) contain binuclear Cu(II) paddlewheel nodes each bridged by four carboxylate centers [21]. These afford desolvated porous materials that incorporate a vacant coordination site at each Cu(II) center and have large pore volumes that contribute to H_2 adsorption as high as 7.78 wt% at 77 K and 60 bar. Neutron powder diffraction studies revealed three adsorption sites for this material: at the exposed Cu(II) coordination site, at the pocket formed by three $\{\text{Cu}_2\}$ paddle wheels, and at the cusp of three phenyl rings. Metal-doped zeolites have also been shown by vibrational and neutron spectroscopy to bind H_2 side-on to vacant metal sites, particularly strongly to the Cu^+ in Cu-ZSM-5 even at room temperature [22]. Silica-supported low-valent titanium systems for hydrogen storage are the subject of a report by Antonelli in this issue.

2. Biomimetic H₂ production, photocatalytic water splitting, and fuel cells

The potential use of hydrogen in future energy storage and delivery systems based on renewable energy sources has spurred interest in many aspects of hydrogen production and utilization as indicated by a number of recent thematic journal issues on this subject [23]. Biomimetic hydrogen production, particularly employing sunlight energy (photocatalysis), is a noble challenge and may take a cue from models of the active site of hydrogenase enzymes coupled with models of nature's various photosystems. As will be discussed below, hydrogenases are billion-year old redox enzymes in microorganisms that catalyze Eq. (6) to either utilize H₂ as an energy source or dispose of excess electrons as H₂.



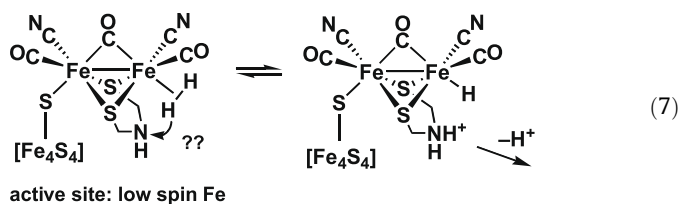
The need for developing methodologies for H₂ production from water is obvious, but also there is necessity for efficient “burning” of hydrogen fuel, i.e. development of efficient inexpensive fuel cells. A fuel cell, much like a battery, obtains electrical energy directly from a chemical reaction, but unlike a battery, electrical power is furnished as long as the reacting chemicals are supplied to each electrode with the cathode receiving oxidant and the anode receiving reductant or “fuel” [24]. The environmental advantages over combustion is clear since fuel cells avoid the high temperatures that cause nitrogen oxide production, and they operate at a higher efficiency (typically 50–60%) than internal combustion engines (20–25%). Aside from environmental driving forces, alternate energy demands continue to drive fuel cell development today. Fuel cells vary greatly in their power output, ranging from large-scale (kW) building-integrated systems to those designed for small-scale devices. The power output of a fuel cell can be limited by the electrochemical reactions occurring at either of the two electrodes, the anode for oxidizing fuel and the cathode for reducing oxidant. Thus the electrodes are usually coated with electrocatalysts, which are often transition-metal based.

Of particular interest for the production and utilization of hydrogen is the development of new electrocatalysts that are *not based on platinum or other precious metals*. Current polymer electrolyte membrane (PEM) fuel cells use platinum as the catalyst for both half reactions, oxidation of hydrogen and reduction of oxygen, but platinum is expensive. Structural studies of hydrogenase enzymes have shown that abundant, inexpensive metals such as nickel and iron are capable of catalyzing the efficient oxidation and production of hydrogen [25–28]. This has led to a wealth of studies to mimic the structure and function of these enzymes with much smaller molecular complexes [23,29–37] and to the development of synthetic catalysts that are functional but not structural

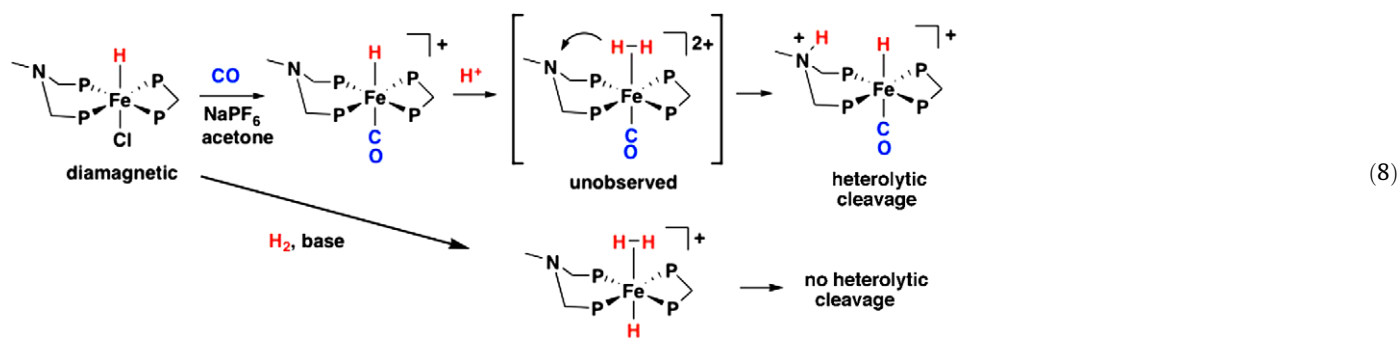
are included in this issue, as reported by Artero, Capon, Evans, Heinekey, and De Gioia.

A recent tactic is use of an *enzyme fuel cell*, which uses a hydrogenase enzyme as the electrocatalyst, either at both cathode and anode, or at just one of the electrodes [24,38]. The catalytic properties of redox enzymes offer advantages in fuel cell applications, although examples of devices exploiting enzyme electrocatalysis are almost exclusively at a “proof of concept” stage. Not only are enzymes capable of very high activity (on a per mole basis), but also they are usually highly selective for their substrates. This simplifies fuel cell design because fuel and oxidant need not be separated (e.g. by an ionically conducting membrane) and can be introduced as a mixture, that is, mixed reactant fuel cells are possible. The main disadvantage of enzymes is their very large size; hence multilayers of enzyme are likely to be needed to provide sufficient current. Also, enzymes are often unstable outside ambient conditions of temperature and pH, and long-term durability is difficult to achieve. However, research on enzyme electrocatalysis will provide inspiration for development of better synthetic catalysts.

Astonishingly, structural and spectroscopic studies have shown that biologically unprecedented CO and CN ligands are present in dinuclear active sites of hydrogenases [26–28,39] that are remarkably organometallic-like and have been extensively modeled for biomimetic H₂ production [23,29–32,39b–c,40]. Eq. (7) illustrates the active site and proposed H₂ splitting process for the di-iron hydrogenases.



H₂ binds most likely at a site *trans* to bridging CO and a proton transfers to a basic site such as the putative bridging amine shown in Eq. (7) [39b,c], much as in the “proton relay” complexes studied by DuBois and coworkers [34–37]. Here nickel [34], iron [35], and cobalt [36] diphosphine complexes with non-coordinating pendant amine bases incorporated into the backbone of the ligands (“proton relays”) perform several functions potentially important in the catalytic oxidation or formation of H₂, as well as other processes that require multiple electron/proton transfers. Eq. (8) illustrates proton transfer that notably is facilitated when the H₂ is coordinated *trans* to the CO ligand, a key bonding position that favors heterolytic cleavage.

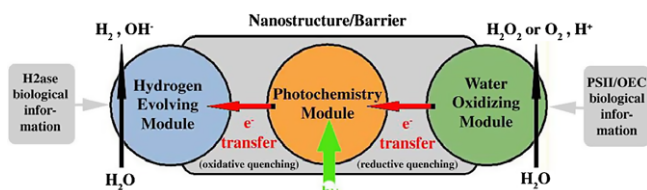


mimics of the enzymes [33]. Efforts to model the structure and function of hydrogenases both experimentally and theoretically

The roles of the proton relays in these synthetic complexes have included stabilizing the binding of to the metal center, assisting the

heterolytic cleavage of coordinated dihydrogen, facilitating intra- and intermolecular proton transfer, and coupling proton and electron transfer events [37]. As a result, Ni and Co complexes containing diphosphine ligands with amine bases in the second coordination sphere exhibit much higher catalytic rates and lower overpotentials for H₂ production and oxidation than analogous compounds lacking these proton relays. Much effort is taking place in designing similar systems involving heterolytic processes aided by complexes containing Lewis basic sites, including coordinated N-donor ligands.

Electron transfer and further deprotonation completes the splitting of H₂, a catalytic cycle which can be reversed in some hydrogenases to produce H₂ from protons and electrons. Biomimetic H₂ production, particularly solar driven (photocatalysis), is desirable and may take a cue from modeling of the active site of hydrogenase and photosystems and coupling these model systems [1,40]. Formation of H–H bonds from protons and electrons, the microscopic reverse of H₂ heterolysis, will be crucial in production of H₂ and is very rapid at the Fe sites in hydrogenases. Coupling model catalysts with photochemical water splitting is being investigated by several groups [40], for example using a scheme shown below.



Water would be oxidized in the right module in a molecular system mimicking biological photosystem II and electrons transferred to a hydrogen-evolving module mimicking hydrogenase. Most of the efforts on modeling hydrogenase activity have been on bimetallic systems, but monometallic complexes should also catalyze dihydrogen production as shown for example in the extensive work by DuBois and coworkers [34–36]. Electrons could be supplied to a hydrogenase model complex by the photochemical module, e.g. the well known Ru(bipyridyl)₃ type systems, possibly via a “molecular wire” linker, e.g. unsaturated C–C bonds or phenyl groups such as studied by the groups of Sun and Artero [40b,c,f]. Wang and coworkers report in this issue new approaches to photochemical H₂ production catalyzed by polypyridyl ruthenium–cobaloxime heterobinuclear complexes.

The other half of the cycle, water oxidation to form oxygen, is actually more of a challenge. A recent report by Milstein and coworkers describes consecutive thermal H₂ and light-induced O₂ evolution from water promoted by a organometallic ruthenium “pincer” hydride complex that establishes a novel multi-step process towards both hydrogen and dioxygen generation in a single homogeneous system [41]. Although not catalytic, the fact that a simple molecular system can accomplish water splitting is thought provoking and holds hope for future development of organometallic systems for energy production.

References

- [1] N.S. Lewis, D.G. Nocera, PNAS 103 (2006) 15729.
- [2] Chem. Eng. News, April 13, 2009, p. 46.
- [3] N. Sutin, C. Creutz, E. Fujita, Comments Inorg. Chem. 19 (1997) 67.
- [4] (a) G.J. Kubas, R.R. Ryan, B.I. Swanson, P.J. Vergamini, H.J. Wasserman, J. Am. Chem. Soc. 106 (1984) 451; (b) G.J. Kubas, Metal Dihydrogen and σ -Bond Complexes, Kluwer Academic/Plenum Publishers, New York, 2001.
- [5] D.G. Hamilton, R.H. Crabtree, Adv. Organomet. Chem. 28 (1988) 299.
- [6] G.J. Kubas, Chem. Rev. 107 (2007) 4152.
- [7] R. Noyori, Angew. Chem., Int. Ed. 41 (2002) 2008.
- [8] D.J. Evans, C.J. Pickett, Chem. Soc. Rev. 32 (2003) 268.
- [9] G.J. Kubas, J. Organomet. Chem. 635 (2001) 37.
- [10] F. Maseras, A. Lledós, E. Clot, O. Eisenstein, Chem. Rev. 100 (2000) 601.
- [11] T. Hasegawa, Z. Li, S. Parkin, H. Hope, R.K. McMullan, T.F. Koetzle, H. Taube, J. Am. Chem. Soc. 116 (1994) 4352.
- [12] N. Aebischer, U. Frey, A.E. Merbach, Chem. Commun. (1998) 2303.
- [13] (a) R.H. Morris, in: M. Peruzzini, R. Poli (Eds.), Recent Advances in Hydride Chemistry, Elsevier Science B.V., Amsterdam, 2001, p. 1; (b) G.J. Kubas, Adv. Inorg. Chem. 56 (2004) 127.
- [14] M. Besora, A. Lledós, F. Maseras, Chem. Soc. Rev. 38 (2009) 957.
- [15] (a) G.C. Welch, R.R. San Juan, J.D. Masuda, D.W. Stephan, Science 314 (2006) 1124; (b) S.J. Geier, T.M. Gilbert, D.W. Stephan, J. Am. Chem. Soc. 130 (2008) 12632; (c) D.W. Stephan, Dalton Trans. (2009); (d) M. Ullrich, A.J. Lough, D.W. Stephan, J. Am. Chem. Soc. 131 (2009) 52.
- [16] D.E. Schwarz, T.M. Cameron, P.J. Hay, B.L. Scott, W.T. Tumas, D.L. Thorn, Chem. Commun. (2005) 5919.
- [17] (a) R.D. Adams, B. Captain, Angew. Chem., Int. Ed. 47 (2008) 252; (b) R.D. Adams, B. Captain, Acc. Chem. Res. 42 (2009) 409.
- [18] F.H. Stephens, V. Pons, R.T. Baker, Dalton Trans. (2007) 2613.
- [19] (a) N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keefe, O.M. Yaghi, Science 300 (2003) 1127; (b) J.L.C. Rowsell, J. Eckert, O.M. Yaghi, J. Am. Chem. Soc. 127 (2005) 14904; (c) P.M. Forster, J. Eckert, B.D. Heiken, J.B. Parise, J.W. Yoon, S.W. Jung, J.-S. Chang, A.K. Cheetham, J. Am. Chem. Soc. 128 (2006) 16846; (d) F. Nouar, J. Eckert, J.E. Eubank, P. Forster, M. Eddaoudi, J. Am. Chem. Soc. 131 (2009) 2864; (e) S. Ma, J. Eckert, P.M. Forster, J.W. Yoon, Y.K. Hwang, J.-S. Chang, C.D. Collier, J.B. Parise, H.-C. Zhou, J. Am. Chem. Soc. 130 (2008) 15896.
- [20] (a) T.K.A. Hoang, D.M. Antonelli, Adv. Mater. 21 (2009) 1787; (b) K.M. Thomas, Dalton Trans. (2009) 1487; L.J. Murray, M. Dinca, J.R. Long, Chem. Soc. Rev. 38 (2009) 1284.
- [21] X. Lin, I. Telepeni, A.J. Blake, A. Dailly, C.M. Brown, J.M. Simmons, M. Zoppi, G.S. Walker, K.M. Thomas, T.J. Mays, P. Hubberstey, N.R. Champness, M. Schroder, J. Am. Chem. Soc. 131 (2009) 2159.
- [22] P.A. Georgiev, A. Albinati, B.L. Mojet, J. Ollivier, J. Eckert, J. Am. Chem. Soc. 129 (2007) 8086.
- [23] (a) W. Lubitz, W. Tumas (Eds.), Chem. Rev. 107 (2007) 3899; (b) P. Schollhammer, J. Talarmin (Eds.), C. R. Chim. 11 (2008) 789; (c) C.J. Pickett, S.P. Best (Eds.), Coord. Chem. Rev. 249 (2005) 1517.
- [24] J.A. Cracknell, K.A. Vincent, F.A. Armstrong, Chem. Rev. 108 (2008) 2439.
- [25] (a) M. Frey, ChemBioChem 3 (2002) 153; (b) J.W. Peters, Curr. Opin. Struct. Biol. 9 (1999) 670.
- [26] J.W. Peters, W.N. Lanzilotta, B.J. Lemon, L.C. Seefeldt, Science 282 (1998) 1853.
- [27] Y. Nicolet, A.L. de Lacey, X. Vernède, V.M. Fernandez, E.C. Hatchikian, J.C. Fontecilla-Camps, J. Am. Chem. Soc. 123 (2001) 1596.
- [28] J.C. Fontecilla-Camps, A. Volbeda, C. Cavazza, Y. Nicolet, Chem. Rev. 107 (2007) 4273.
- [29] (a) B.E. Barton, M.T. Olsen, T.B. Rauchfuss, J. Am. Chem. Soc. 130 (2008) 16834; (b) F. Gloaguen, T.B. Rauchfuss, Chem. Soc. Rev. 38 (2009) 100.
- [30] T. Liu, M.Y. Darensbourg, J. Am. Chem. Soc. 129 (2007) 7008.
- [31] S. Löscher, L. Schwartz, M. Stein, S. Ott, M. Haumann, Inorg. Chem. 46 (2007) 11094.
- [32] V. Artero, M. Fontecave, Coord. Chem. Rev. 249 (2005) 1518.
- [33] (a) X. Hu, B.S. Brunschwig, J.C. Peters, J. Am. Chem. Soc. 129 (2007) 8988; (b) X.L. Hu, B.M. Cossairt, B.S. Brunschwig, N.S. Lewis, J.C. Peters, Chem. Commun. (2005) 4723; (c) P. Connolly, J.H. Espenson, Inorg. Chem. 25 (1986) 2684; (d) C. Baffert, V. Artero, M. Fontecave, Inorg. Chem. 46 (2007) 1817; (e) A.M. Appel, D.L. DuBois, M. Rakowski DuBois, J. Am. Chem. Soc. 127 (2005) 12717.
- [34] (a) C.J. Curtis, A. Miedaner, R.F. Ciancanelli, W.W. Ellis, B.C. Noll, M. Rakowski DuBois, D.L. DuBois, Inorg. Chem. 42 (2003) 216; (b) A.D. Wilson, R.H. Newell, M.J. McNevin, J.T. Muckerman, M. Rakowski DuBois, D.L. DuBois, J. Am. Chem. Soc. 128 (2006) 358; (c) A.D. Wilson, A. Miedaner, J.T. Muckerman, D.L. DuBois, M. Rakowski DuBois, Proc. Nat. Acad. Sci. USA 104 (2007) 6951; (d) K. Frazee, A.D. Wilson, A.M. Appel, M. Rakowski DuBois, D.L. DuBois, Organometallics 26 (2007) 5003; (e) A.D. Wilson, K. Frazee, B. Twamley, S. Miller, D.L. DuBois, M. Rakowski DuBois, J. Am. Chem. Soc. 130 (2008) 1061; (f) J.Y. Yang, R.M. Bullock, W.J. Shaw, B. Twamley, K. Frazee, M. Rakowski DuBois, D.L. DuBois, J. Am. Chem. Soc. 131 (2009) 5935.
- [35] (a) R.M. Henry, R.K. Shoemaker, R.H. Newell, G.M. Jacobsen, D.L. DuBois, M. Rakowski DuBois, Organometallics 24 (2005) 2481; (b) R.M. Henry, R.K. Shoemaker, D.L. DuBois, M. Rakowski DuBois, J. Am. Chem. Soc. 128 (2006) 3002; (c) G.M. Jacobsen, R.K. Shoemaker, M. Rakowski DuBois, D.L. DuBois, Organometallics 26 (2007) 4964; (d) G.M. Jacobsen, R.K. Shoemaker, M.J. McNevin, M. Rakowski DuBois, D.L. DuBois, Organometallics 26 (2007) 5003.
- [36] G.M. Jacobsen, J. Yang, B. Twamley, A.D. Wilson, R.M. Bullock, M. Rakowski DuBois, D.L. DuBois, Energ. Environ. Sci. 1 (2008) 167.
- [37] (a) M. Rakowski DuBois, D.L. DuBois, C. R. Chim. 11 (2008) 805; (b) M. Rakowski DuBois, D.L. DuBois, Chem. Soc. Rev. 38 (2009) 62.

- [38] E. Reisner, J.C. Fonticella-Camps, F.A. Armstrong, *Chem. Commun.* (2009) 550.
- [39] (a) A. Volbeda, J.C. Fonticella-Camps, *Coord. Chem. Rev.* 249 (2005) 1609;
(b) X. Liu, S.K. Ibrahim, C. Tard, C.J. Pickett, *Coord. Chem. Rev.* 249 (2005) 1641;
(c) M.Y. Darensbourg, E.J. Lyon, Z. Zhao, I.P. Georgakaki, *PNAS* 100 (2003) 3683.
- [40] (a) J.-F. Capon, F. Gloagen, P. Schollhammer, J. Talarmin, *Coord. Chem. Rev.* 249 (2005) 1664;
(b) L. Sun, B. Akermark, S. Ott, *Coord. Chem. Rev.* 249 (2005) 1653;
(c) H. Wolpher, M. Borgdtrom, L. Hammerstrom, J. Bergquist, V. Sundstrom, S. Styring, L. Sun, B. Akermark, *Inorg. Chem. Commun.* 6 (2003) 989;
- (d) J. Alper, *Science* 299 (2003) 1686;
- (e) R.M. Henry, R.K. Shoemaker, R.H. Newell, G.M. Jacobsen, D.L. DuBois, M. Rakowski DuBois, *Organometallics* 24 (2005) 2481;
- (f) A. Fihri, V. Artero, M. Razavet, C. Baffert, W. Leibl, M. Fontecave, *Angew. Chem., Int. Ed.* 47 (2008) 564.
- [41] (a) S.W. Kohl, L. Weiner, L. Schwartsburd, L. Konstantinovski, L.J.W. Shimon, Y. Ben-David, M.A. Iron, D. Milstein, *Science* 324 (2009) 74;
(b) . See also perspective article: R. Eisenberg, *Science* 324 (2009) 44.