Hydrogen Storage

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Storing and Releasing Hydrogen with a Redox Switch**

*Simon K. Brayshaw, Jennifer C. Green, Nilay Hazari, J. Scott McIndoe, Frank Marken, Paul R. Raithby, and Andrew S. Weller**

Hydrogen storage is an area of intense current interest, which is driven by the requirements for reversible storage of dihydrogen for future energy applications.[1] Chemisorption of dihydrogen in the form of light metal hydrides is one approach to the problem of storing large amounts of H_2 reversibly.[2] Physisorption of dihydrogen onto porous network materials such as activated carbon, metal–organic framework (MOF) materials,[3] or related systems[4,5] presents an alternative method, and MOF systems that incorporate open metal sites (such as Ni^{2+}, Cu^{2+}, and Mg^{2+})[5–8] have recently attracted attention because of the stronger binding of H_2 with the metal–ligand framework.[8] Although significant and elegant advances have been made in both areas,

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[*] Dr. S. K. Brayshaw, Dr. F. Marken, Prof. P. R. Raithby, Dr. A. S. Weller
Department of Chemistry
University of Bath
Bath, BA2 7AY (UK)
Fax: (+44) 1225-386-231
E-mail: a.s.weller@bath.ac.uk

Prof. J. C. Green, N. Hazari
Inorganic Chemistry Laboratory
South Parks Road, Oxford OX1 3QR (UK)

Prof. J. S. McIndoe
Department of Chemistry
University of Victoria
PO Box 3065, Victoria, BC V8W3V6 (Canada)

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challenges still remain. Metal hydrides require temperature cycling to promote loss of hydrogen, as hydrogen is chemisorbed (binding energies greater than 100 $\mathrm{kJ\,mol^{-1}}$). Although porous networks show reversible H_2 uptake without temperature cycling, they generally require an overpressure to retain H_2, because reducing the partial pressure results in loss of H_2 (i.e., there is no hysteresis between the absorption and desorption isotherms); this is because dihydrogen is physisorbed[9] (binding energies less than 10 $\mathrm{kJ\,mol^{-1}}$). Although these MOF materials can uptake H_2 very well at 77 K,[7,10] adsorption drops dramatically (less than 0.3 %) at ambient temperature. MOF systems that show hysteresis have been described recently. These materials retain H_2 at reduced pressure (ca. 0.01 atm); however, they only operate at 77 K.[11] In view of the current state of this research, a material that is both a true store of hydrogen under ambient conditions of temperature and pressure and that releases the stored H_2 without significant external energy input would be of fundamental interest.

We report herein what we believe to be a novel mechanism for hydrogen storage and subsequent release. The system consists of molecular clusters in which H_2 is adsorbed at binding energies intermediate between the accepted limits for chemi- and physisorption. These clusters retain the stored dihydrogen even at low pressure, which makes them genuine hydrogen stores, but they can release H_2 rapidly (on the millisecond timescale) when triggered by a simple redox process. Moreover, these processes occur under the attractive conditions of 298 K and 1 atm H_2 and can be triggered either chemically or electrochemically. Although cluster species with hydride ligands are common,[12–17] the reversible uptake and release of H_2 on molecular clusters is rare and examples have generally required relatively forcing conditions (vacuum, heat, photolysis, or addition of an external hydrogen acceptor) to release the stored H_2.[18–20]

We recently reported the synthesis of a new class of rhodium clusters, exemplified by $[\mathrm{Rh_6(PCy_3)_6H_{12}}][\mathrm{BAr^F_4}]_2$ (**A**) ($[\mathrm{BAr^F_4}] = [\mathrm{B\{C_6H_3(CF_3)_2\}_4}]^-$; Cy = cyclohexyl), which have molecular geometries that feature an octahedral hexarhodium core and a trialkyl phosphine ligand radiating from each metal vertex,[19,21,22] thus shrouding the metal core with a hydrocarbon shell. These dicationic clusters are completed by twelve hydrogen atoms that bridge each Rh–Rh edge in the octahedron. Calculations[21] show that there is only a modest energy gap (0.3 eV) between the highest occupied molecular orbital (HOMO) and a degenerate set of two low-lying unoccupied molecular orbitals (LUMOs, Figure 1). Thus, these clusters are predisposed to receive four extra electrons. We have shown that these electrons can come from two H_2 molecules (i.e. two bonding electron pairs) and that the addition of H_2 to **A** affords the 16-hydrogen-atom cluster $[\mathrm{Rh_6(PCy_3)_6H_{16}}][\mathrm{BAr^F_4}]_2$ (**B**), in which the HOMO–LUMO energy gap is much larger (1.3 eV). The uptake of two molecules of H_2 is facile (both in the solution and the solid state) and can be reversed by placing **B** under a dynamic vacuum (ca. 6×10^{-6} atm, $t_{1/2} = 48$ h). Under ambient conditions (1 atm argon, 298 K), cluster **B** retains the two absorbed H_2 molecules for weeks with no partial pressure of H_2.[21]

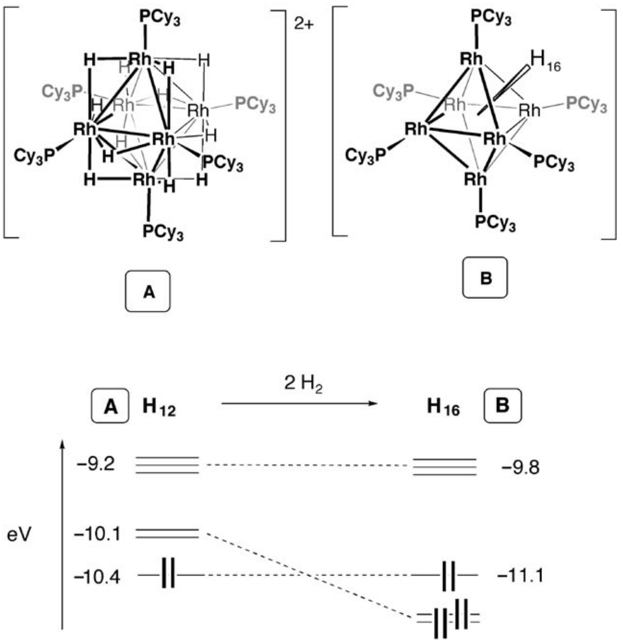

Figure 1. Frontier molecular orbital energy diagram for **A** and **B**.

Inspection of the MO diagram for **B** suggests that the addition of one electron would result in the population of a high-lying orbital and that this could destabilize the cluster, which would result in H_2 loss to reestablish a large HOMO–LUMO gap. Exactly this process does in fact occur, and it can be readily followed chemically and electrochemically by using standard spectroscopic and electrochemical techniques. On a preparative scale the addition of the reducing agent $[\mathrm{Cr(\eta^6\text{-}C_6H_6)_2}]$ ($E_{1/2} = -1.15$ V relative to ferrocene/ferrocenium) to a solution of **B** in $\mathrm{CH_2Cl_2}$ results in a paramagnetic species that we have unequivocally characterized as $[\mathrm{Rh_6(PCy_3)_6H_{14}}][\mathrm{BAr^F_4}]$ (**C**) by following the reaction with electrospray ionisation mass spectrometry (ESI-MS). These spectra show the clean formation of **C**, a monocation with fourteen hydrides associated with a $\{\mathrm{Rh_6(PCy_3)_6}\}$ core (Figure 2). As might be expected, ^{1}H NMR spectroscopy of paramagnetic **C** is relatively uninformative and the hydride signals are not observed. However, H/D exchange experiments using D_2 show the formation of $HD_{(g)}$ and $H_{2(g)}$, which is consistent with accessible dihydrogen ligands on the cluster surface,[23] as are theoretical calculations (see below). Attempts to isolate **C** in pure form on a preparative scale by repeated recrystallization to remove the reductant always led to the loss of H_2 and isolation of the twelve-hydride monocationic cluster $[\mathrm{Rh_6(PCy_3)_6H_{12}}][\mathrm{BAr^F_4}]$ (**D**). The "uncharged-with-H_2" starting material **A** is simply returned by oxidation of **C** with $[\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}][\mathrm{PF_6}]$ ($E_{1/2} = 0.00$ V), as monitored by NMR spectroscopy and ESI-MS. Oxidation of **C** thus results in the elimination of a further equivalent of H_2, and a complete hydrogen store and release cycle is completed in solution for two molecules of H_2 per cluster by a simple redox process.

This redox-triggered release of H_2 can also be followed electrochemically. Figure 3 shows the cyclic voltammogram of **B** (in $\mathrm{CH_2Cl_2}$, $[\mathrm{NBu_4}][\mathrm{BAr^F_4}]$ electrolyte, glassy carbon

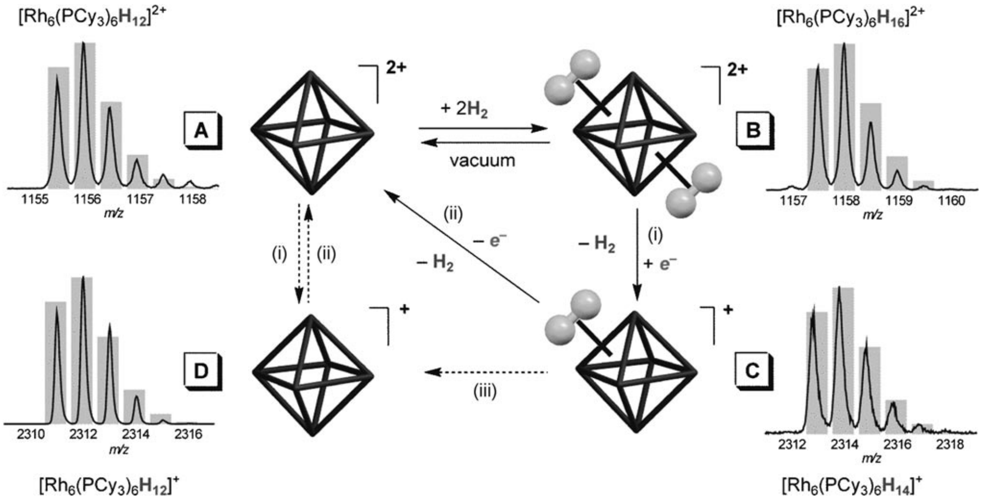

Figure 2. Redox triggered hydrogen storage/release cycle. i) $[Cr(\eta^6\text{-}C_6H_6)_2]$; ii) $[Fe(\eta^5\text{-}C_5H_5)_2][PF_6]$; iii) $-H_2$, glassy carbon electrode. Insets show ESI-MS data (positive-ion mode) of cluster species for each step with the observed isotope pattern overlaid with that predicted (gray bars). See the Supporting Information for full spectra.

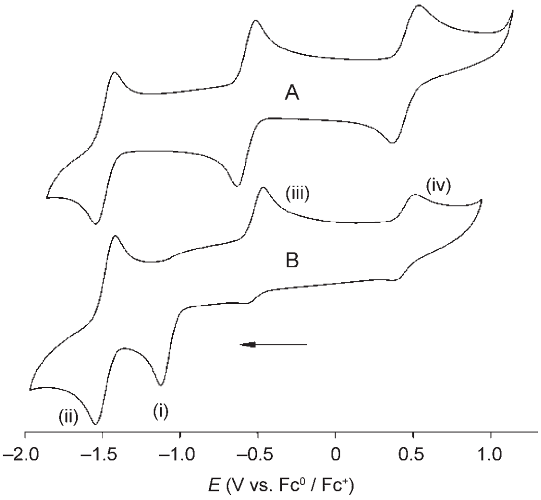

Figure 3. Top: Cyclic voltammogram of $[Rh_6(PCy_3)_6H_{12}]^{2+}$ (**A**) (which is also identical to those of **C** and **D**) showing the three electrochemical processes (two reversible reductions and one quasireversible oxidation). Bottom: Cyclic voltammogram of **B** showing the irreversible reduction (i) and subsequent electrochemistry associated with **A** (ii–iv). See the Supporting Information for full experimental details.

electrode, sweep rate 100 mV s^{-1}). Cluster **B** undergoes an irreversible one-electron reduction at $E_{1/2} = -1.00$ V, relative to ferrocene/ferrocenium, which is consistent with the irreversible elimination of H_2. By progressively increasing the scan rate to 10 V s^{-1} and observing the back oxidation, a half-life for the unstable reduced species of 170 ms ($k = 4\ s^{-}$ at 293 K) was obtained. There are also three reversible one-electron processes at $E_{1/2} = -1.51$, -0.59, and $+0.44$ V, which are also observed for **A**[24] and **D**, the latter related to **C** by the simple loss of one H_2 molecule. Presumably under electrochemical conditions, **C** undergoes facile loss of H_2 to form **D**, and this suggestion is supported by the small calculated energy difference between these two species (0.12 eV, see below) and our observation that H_2 is slowly lost from **C** in bulk solution. Cluster **D** can be formed independently in excellent yield by chemical reduction of **A** with $[Cr(\eta^6\text{-}C_6H_6)_2]$ (see the Supporting Information for full characterization, including the X-ray crystal structure). Overall, the electrochemical behavior of **B** can be summarized as the irreversible loss of two molecules of H_2 upon reduction at the carbon electrode to give **D**, which is directly related to the starting cluster **A** by simple oxidation. Although there is a subtle change in the order of events between the bulk chemical and electrochemical processes, the overall redox hydrogen storage/release cycle holds for both: the reduction of **B** and subsequent reoxidation to afford **A** is effectively quantitative, repeatable, and involves two equivalents of H_2 per cluster per cycle.

Full geometry optimizations and calculations of the relative Gibbs free energies were performed using density functional theory (DFT) (see the Supporting Information for details) on the model system $[Rh_6(PH_3)_6H_x]^{n+}$ ($x = 12, 14, 16$; $n = 1, 2$). The relative energies of the possible intermediates in this cycle (Gibbs free energy at 298.15 K, taking into account solvent effects (CH_2Cl_2), zero-point energy, and entropy) are shown in Figure 4. The addition of two molecules of H_2 to $[H_{12}]^{2+}$ (**A**) to give $[H_{16}]^{2+}$ (**B**) is an overall exothermic process, which is consistent with the experimentally observed formation of **B** on exposure to H_2 (the "charged-with-H_2"

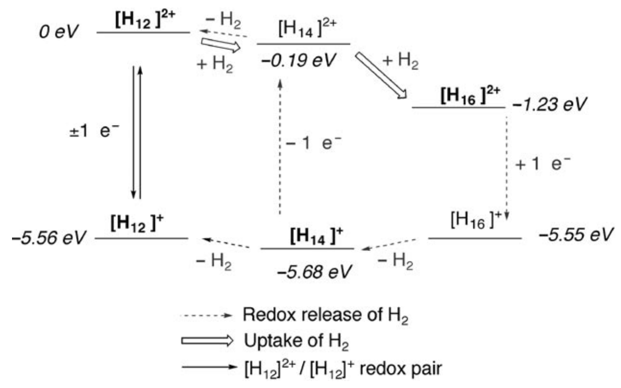

Figure 4. Calculated energies (eV) relative to **A** ($[H_{12}]^{2+}$) for the cluster hydride species in the storage/release cycle. Molecular species in bold face were observed spectroscopically and in some cases [**A**, **B**,[21] and **D** (this work)] determined by X-ray diffraction. Energies quoted take into account the Gibbs free energy of gaseous H_2 where appropriate. PCy_3 was replaced by PH_3 in the model systems.

state). A reasonable supposition is that this proceeds via an intermediate dicationic species with fourteen hydrides, namely $[Rh_6(PH_3)_6H_{14}]^{2+}$ ($[H_{14}]^{2+}$). The average interaction energy of the two extra H_2 molecules with the cluster was determined to be 0.62 eV (60 kJ mol^{-1}) per dihydrogen. This is comparable with the binding energy both calculated and experimentally determined for dihydrogen bound to a single metal center (60–100 kJ mol^{-1}),[23] and DFT calculations and H/D exchange experiments both strongly suggest two dihydrogen ligands on the cluster surface of this sixteen-hydride species.[21] Addition of one electron to $[H_{16}]^{2+}$ results in $[Rh_6(P(PH_3)_3)_6H_{16}]^+$ ($[H_{16}]^+$), which is unstable towards H_2 loss to afford $[H_{14}]^+$ and H_2. The calculated structure of $[H_{14}]^+$ reveals a relatively close H–H contact on the cluster surface (1.06 Å), which is suggestive of a dihydrogen ligand. Oxidation of $[H_{14}]^+$ yields $[Rh_6(PH_3)_6H_{14}]^{2+}$ ($[H_{14}]^{2+}$). Although this species is marginally lower in energy than $[H_{12}]^{2+}$, there must be only a small barrier towards H_2 loss, which can be overcome simply by loss of hydrogen to the bulk solution. The barrier to loss of H_2 from $[H_{14}]^+$ must be larger, as cluster **C** is observed experimentally in bulk solution by ESI-MS. Although the precise mechanism of H_2 loss is currently uncertain, the correlation between experiment and theory is reasonable, especially given that the approximations involved in using PH_3 instead of PCy_3 mean that kinetic factors towards H_2 loss may not be modeled accurately. Importantly, the experimental observations show unequivocally that the overall hydrogen storage/release cycle ($\mathbf{A}\rightleftarrows\mathbf{B}$) involves two molecules of H_2 per cluster irrespective of the precise mechanistic details.

The hydrogen storage capacity of **A** (0.1 % w/w) is modest, as the cluster and associated anions have high molecular mass, and this value is clearly not sufficient for practical purposes (the US Department of Energy 2010 target is 6 % w/w [25]). However, the ability to store H_2 without a partial pressure of H_2 (and even under dynamic vacuum) at 298 K, coupled with the very rapid redox-promoted release of H_2, is unique. These attractive features result from the electronic and steric properties of the metal cluster, namely: 1) two low-lying unoccupied molecular orbitals available for the uptake of bonding electron pairs from H_2; 2) the resulting calculated binding energy of H_2 to the cluster of 60 kJ mol^{-1} (lying at a value intermediate between physi- and chemisorption regimes); and 3) the kinetic stabilization afforded against facile hydrogen loss by the trialkyl phosphine groups. These results suggest that future strategies involving redox-switchable metal clusters in hydrogen storage materials or hydrogen spillover systems[26] could well prove worthwhile.

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