

Reversible Binding of Dihydrogen in Multimetallic Complexes

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The interaction of hydrogen with metal surfaces is one of the most important and fundamental processes in the chemical industry. Hydrogen is also strongly tipped to play a central role in new challenges that are emerging in terms of climate change and energy supply, and the reversible binding of H₂ to suitable materials will play a keystone role in the realisation of the hydrogen economy. The reversible interaction of hydrogen with multimetallic centres is also an important theme in biological processes; the role of hydrogenases in the metabolism of H₂ is an example. Thus the reversible interaction of H₂ with multimetallic metal complexes is an area that spans considerable breadth. This review is concerned

with the reversible interaction of H₂ with soluble multimetallic complexes, defined broadly as clusters, in which there are no other ligands lost or gained in the process. The review is organised under the subheadings: equilibrium reversible (H₂ is lost upon removal of the H₂ atmosphere), thermally reversible or reversible when placed under vacuum, photochemically reversible and electrochemically reversible interactions; a brief outline of reversible H₂ binding in systems of biological interest; giant metal clusters that display reversible H₂ binding.

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Introduction

The interaction of hydrogen with metal surfaces is one of the most important and fundamental processes in the

chemical industry. Catalytic hydrogenations are the largest chemical reactions by volume, as all crude oil is treated with H₂ in desulfurisation, while ammonia production from N₂ and H₂ over an iron oxide catalyst produces ammonia fertiliser on a multimillion tonne scale per year. Both of these processes involve heterogeneous metal catalysts and accordingly the interaction of hydrogen with a metal surface. Hydrogen is also strongly tipped to play a central role in new challenges that are emerging in terms of climate change and energy supply, in that it is a valuable future fuel that when burnt (either in a combustion engine or a fuel cell) releases only water. It is widely accepted that the realisation of the

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Andrew Weller completed his first degree at the University of Warwick and his PhD at the University of Bristol (1994) under the supervision of Dr John Jeffery. After postdoctoral positions with Professor Alan Welch (Heriot-Watt University) and Professor Thomas Fehlner (University of Notre Dame) he returned to the UK and took up a Royal Society University Research Fellowship at the University of Bath in 1999. He was promoted to Reader in 2004. In September 2007 he moved to the Department of Chemistry University of Oxford. His research broadly covers synthetic organometallic chemistry, catalysis and structure and bonding. Major research themes in his group are: (i) the synthesis of high-hydride-content rhodium clusters (and their precursors) and (ii) the transition-metal chemistry of low-coordinate cationic late-transition-metal complexes, especially those incorporating weakly coordinating anions, for use in catalysis and C–H/C–C activation processes.



Scott McIndoe was born and educated in New Zealand. He completed his DPhil in synthetic (in)organometallic chemistry at the University of Waikato under the supervision of Professor Brian Nicholson. In 1998, he won a New Zealand Foundation for Research, Science & Technology Postdoctoral Fellowship and joined the group of Professor Brian Johnson FRS at the University of Cambridge (UK). In 2000, he took up a college lectureship, teaching at Trinity and Newnham Colleges, Cambridge, and continued his research in the Department of Chemistry. Three years later he moved to his current position, as assistant professor in the Department of Chemistry at the University of Victoria, where his research group uses mass spectrometry as a rapid discovery tool in organometallic chemistry and catalysis.

“hydrogen economy”^[1] will require breakthroughs in the crucial area of efficient storage of hydrogen accompanied with favourable charge/discharge kinetics and operating temperatures.^[2] Although they are not the only possible solution, metal complexes of hydrogen could well make important contributions to the realisation of this goal; even though it is highly unlikely that a practicable solution to store H₂ would involve metal complexes from the second or third rows with attached ligands – a consequence of the combined factors of very low %H content and cost. The study of the reversible interaction of hydrogen with metal surfaces and other materials is an area that has been occupying molecular and solid-state chemists, surface scientists and physicists for many years, and the level of interest in this field remains high.

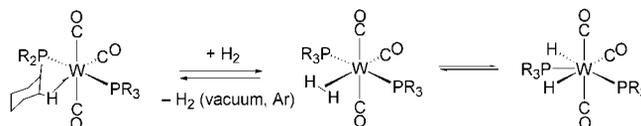
This review is concerned with the reversible interaction of H₂ with well-defined multimetallic soluble complexes, defined broadly as clusters. Reversibility in this context suggests that there is no other change in formulation to the cluster material on addition or removal of H₂, meaning that there must be no other ligands lost or gained in the process. The consequence of this stipulation is that reversible uptake of H₂ in multimetallic systems without ligand displacement must occur on a molecule that has available low lying orbitals to take up the bonding pairs of H₂ – in other words the system must be formally electronically (and most likely coordinatively) unsaturated or have access to such a state by ligand or metal-core rearrangement. The review limits itself to well-defined molecular systems, venturing briefly into nearly monodisperse nanoclusters but avoiding larger metal particles, surfaces and bulk metals except for the purpose of comparison.

Hydrogen–Transition–Metal Bonding

Hydrogen may either chemisorb on a metal surface as atomic hydrogen or physisorb as an intact H₂ molecule. Both have parallels in molecular cluster chemistry: metal hydrides and metal dihydrogen complexes, respectively. Detecting hydrogen bound to a metal surface is not straightforward and requires the use of a limited set of high-vacuum techniques, such as electron energy loss spectroscopy (EELS) or scanning tunnelling microscopy (STM).^[3] Information obtained from such experiments shows that on a metal(111) surface atomic hydrogen adsorbs to form a monolayer of hydrogen at 37 K, and the H atoms are chemisorbed on threefold face-centred cubic sites, positioned in the hollows between the metal atoms. Binding of intact H₂ to nanoclusters and metal surfaces is rare because of the preferential formation of hydrides,^[4,5] although there is evidence for dihydrogen bound to a Ni(510) surface.^[6] In the molecular realm, the interaction of atomic hydrogen with metal clusters (hydride ligands) is very well documented, and there are literally thousands of examples of metal hydride cluster species.^[7] By contrast, the coordination of molecular hydrogen in complexes with multimetallic systems is considerably less common, and to the best of our

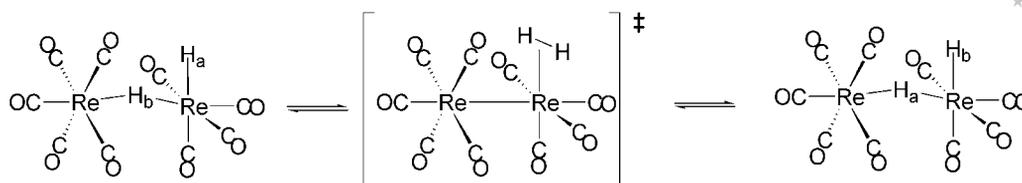
knowledge only a handful of examples exist in which a relatively reliable indicator such as a short *T*₁ relaxation time associated with the bound dihydrogen has been reported.^[8–12]

The exemplar for dihydrogen coordination to soluble metal complexes remains the original Kubas complex W(PR₃)₂(CO)₃ (R = Cy, *i*Pr), in which an agostic C–H–M interaction from a bulky cyclohexyl group provides light stabilisation of the metal centre, allowing for an operationally unsaturated 16-electron complex. Addition of H₂ displaces this interaction to form the, now classic, complex W(PR₃)₂(CO)₃(η²-H₂) (R = Cy, *i*Pr) (Scheme 1). Placing this compound under a non-hydrogen atmosphere or vacuum removes the bound H₂ and re-establishes the agostic C–H bond.^[5,13] These dihydrogen complexes are also in equilibrium in solution with the tautomeric dihydride forms (the dihydrogen complexes are favoured), and the Δ*G*[‡] for this oxidative addition of H₂ has been estimated to be 60 kJ mol⁻¹. The equilibrium demonstrates an important point in that even though a dihydride is observed as the major (or often the only) species by NMR spectroscopy and X-ray crystallography, a low-energy pathway to a coordinated dihydrogen ligand can allow for the loss of H₂. If the resulting complex is stabilised in the absence of H₂ by either steric bulk and/or agostic interactions, then the molecule is available to take up H₂ again without decomposition. Examples of H₂ loss in mononuclear complexes where the resulting molecule is unstable and dimerises to relieve the unsaturation are known, but we do not focus on these here.^[10]



Scheme 1. R = Cy.

Although examples of multimetallic complexes where dihydride and dihydrogen complexes are in slow equilibrium with one another are not known, computational and experimental studies indicate that such a transformation is likely to have a comparable barrier to those determined for mononuclear complexes. For example, the rapid H/D exchange in CpRu(μ-H)₄RuCp on addition of D₂ is calculated as passing through a dihydrogen transition state with a rate-determining barrier of less than 80 kJ mol⁻¹.^[14] The dihydride complex Re₂H(μ-H)(CO)₉ irreversibly loses H₂ above 253 K and is a highly fluxional molecule, exchanging hydride sites through a low-energy process (Scheme 2).^[15] NMR spectroscopic data (*T*₁ measurements) suggest a dihydride structure; however, experimental and theoretical studies are in close agreement and show that the barrier for exchange through a dihydrogen intermediate is only 23 and 27 kJ mol⁻¹, respectively. (η²-H₂)(isoPFA)Ru(μ-Cl)₂(μ-H)-RuH(PPh₃)₂ undergoes rapid exchange between dihydrogen and bridging dihydride ligands at 20 °C (barrier 53 kJ mol⁻¹)^[8,16] as do related chelated phosphane complexes^[12] and the cluster [Ru₄(η⁶-C₆H₆)₄H₆]²⁺,^[11] both of which have a mixture of dihydrogen and dihydride ligands



Scheme 2.

as characterised by T_1 relaxation time measurements by NMR spectroscopy at low temperature. The iridium dimer $\text{Ir}_2(\text{P}i\text{Pr}_3)_2(\text{pz})_2(\text{H})_2(\mu\text{-H})(\eta^2\text{-H}_2)$ is suggested to have a dihydrogen ligand that undergoes rapid exchange with a terminal hydride, with a barrier of 32 kJ mol^{-1} .^[17] Mechanisms for hydride/dihydrogen exchange have recently been reviewed in the more general sense of exchange mechanisms in sigma complexes.^[18]

In mononuclear complexes hydrogen is found either as a hydride ligand (H) or as dihydrogen ($\eta^2\text{-H}_2$). The H–H distance defines the difference between a true H_2 complex ($0.8\text{--}1.0 \text{ \AA}$) and a dihydride ($> 1.6 \text{ \AA}$),^[5] with intermediate H–H lengths described as elongated H_2 complexes or compressed dihydrides.^[19] In polynuclear metal clusters, however, hydrogen may occupy a variety of different positions with respect to the metal centres that are not available to mononuclear complexes, including bridging, face-bridging and interstitial locations (Figure 1).

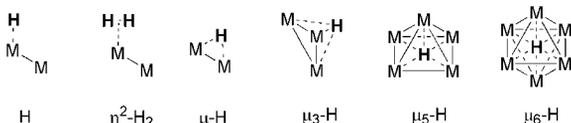


Figure 1. Hydrogen bonding modes observed in cluster complexes; terminal hydride (H), dihydrogen complex ($\eta^2\text{-H}_2$), bridging hydride ($\mu\text{-H}$), face-bridging hydride ($\mu_3\text{-H}$) and interstitial hydrides ($\mu_5\text{-H}$ and $\mu_6\text{-H}$).

Neutron diffraction studies are the definitive structural answer to the exact mode of hydrogen coordination, and all of the cluster-only ($\mu_n\text{-}$) binding modes have been unambiguously characterised by this method; examples include ($\mu\text{-H}$) $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-CCCMe}_3)$,^[20] ($\mu_3\text{-H}$) $_4\text{Co}_4(\eta^5\text{-C}_5\text{Me}_4\text{-Et})_4$,^[21] [$\mu_5\text{-H}$] $_2\text{Rh}_{13}(\text{CO})_{24}$ ^[22] and [$\mu_6\text{-H}$] $\text{Ru}_6(\text{CO})_{18}$.^[23] However, terminal hydride and dihydrogen ligands are sufficiently rare in cluster chemistry, and they remain uncharacterised by neutron diffraction. An unusually well-characterised example of a bimetallic species with a dihydrogen ligand is $(\eta^2\text{-H}_2)(\text{isoPFA})\text{Ru}(\mu\text{-Cl})_2(\mu\text{-H})\text{RuH}(\text{PPh}_3)_2$ (isoPFA = $\{\eta^5\text{-C}_5\text{H}_5\}\text{Fe}(\eta^5\text{-C}_5\text{H}_3(\text{CHMeNMe}_2)\text{-P}i\text{Pr}_2)\}$), which was investigated by X-ray crystallography and variable-temperature ^1H - and ^{31}P -NMR spectroscopy.^[8] The structure (Figure 2) is notable for having three different binding modes of H present in one structure. The NMR spectroscopic data for this compound revealed fast exchange between the $\eta^2\text{-H}_2$ and the $\mu\text{-H}$ at $20 \text{ }^\circ\text{C}$ and a slower exchange of these three hydrogen atoms with the terminal hydride.

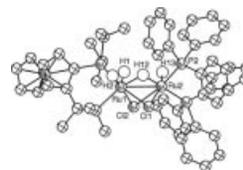


Figure 2. X-ray crystal structure of $(\eta^2\text{-H}_2)(\text{isoPFA})\text{Ru}(\mu\text{-Cl})_2(\mu\text{-H})\text{RuH}(\text{PPh}_3)_2$.^[8]

In almost all instances, addition of hydrogen to a metal cluster is preceded or accompanied by ligand dissociation to generate a coordinatively and electronically unsaturated^[24] cluster to which H_2 can be added. For example, addition of H_2 to $\text{Os}_3(\text{CO})_{12-n}(\text{NCMe})_n$ ($n = 1, 2$) occurs by NCMe dissociation and addition of H_2 to form $\text{Os}_3(\text{CO})_{10-n}(\mu\text{-H})_2$.^[25] For unsaturated metal clusters, often decorated with bulky phosphane ligands such as PtBu_3 , PCy_3 and $\text{P}i\text{Pr}_3$, ligand dissociation is not a prerequisite for addition of H_2 . These ligands provide a steric shield around the metal centre that prevents ligands other than the smallest molecules, such as H_2 , from easily entering the coordination sphere of the cluster (see Figure 3). Thus these clusters are kinetically stabilised with respect to addition of further ligands. As will be shown, these unsaturated complexes often have low-lying unoccupied molecular orbitals that show small HOMO–LUMO gaps and are well set up for uptake of electrons from the H_2 bonding pairs.

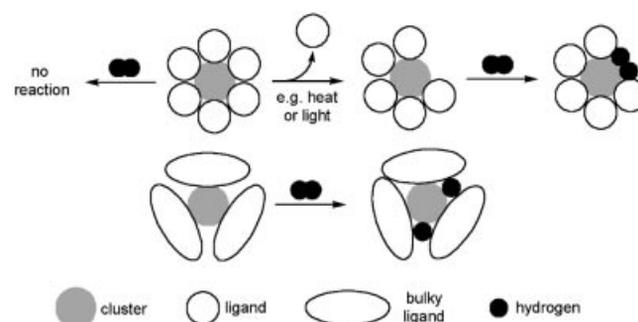


Figure 3. Cartoon showing (top) how most multimetallic compounds require ligand loss prior to hydrogen binding and (bottom) how electronically unsaturated compounds with bulky ligands escape this requirement and can frequently bind hydrogen reversibly without significant structural change.

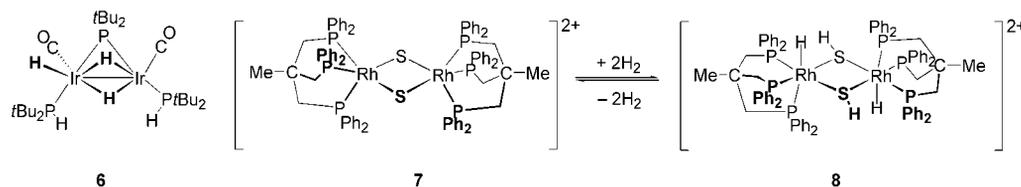
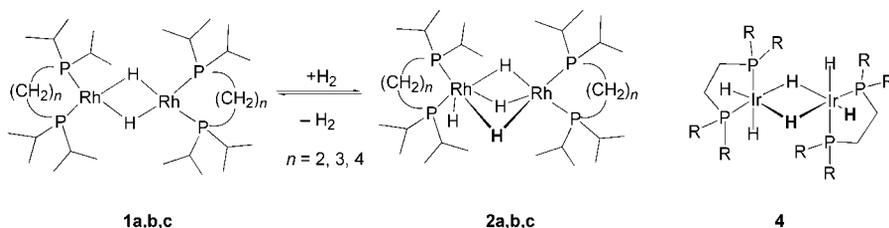
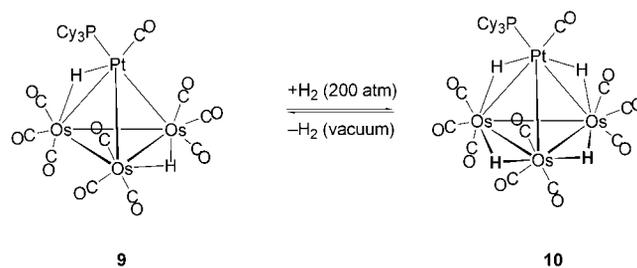
Equilibrium Reversible (H_2 Is Lost upon Removal of the H_2 Atmosphere)

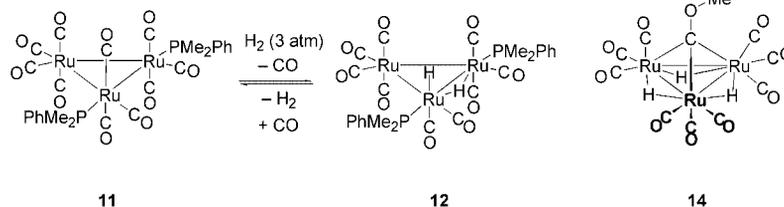
Many unsaturated multimetallic complexes add H_2 to give hydride species, but often this is a reversible process, and removal of the H_2 atmosphere regenerates the starting material. Given that hydrogen addition and loss are clearly low-energy processes, in these examples it is not surprising to find that many of these complexes also undergo rapid H/D exchange when placed under a D_2 atmosphere.

Muetterties, and later Fryzuk, reported that addition of H_2 to the unsaturated (28 electrons) dimeric complexes $[L_2Rh_2(\mu-H)_2]$ (**1a–e**) ($L = iPr_2P(CH_2)_nPiPr_2$ $n = 2$ **1a**; **3 1b**; **4 1c**;^[26] $L = PiOPr_3$ **1d**, $L = POMe$ **1e**^[27]) results in the complexes $[L_2Rh_2(\mu-H)_3H]$ (**2a–e**), which are best formulated as having Rh^{III}/Rh^I metal centres and have been characterised spectroscopically.^[26] For the chelating ligand **2c** with the largest bite angle, the extra hydrides are held quite firmly – even under vacuum – and require an acceptor (1-hexene) to remove H_2 . For the ligands **2a** and **2b** with smaller bite angles, the hydrogen is lost on removal of the H_2 atmosphere. The ligand in **2c** presumably shields the metal centres more effectively and kinetically blocks H_2 loss. This reasoning we will return to later, and steric blocking seems important in both the generation and stabilisation of hydrogen-rich complexes. Large ligands block the approach of additional large ligands that would satisfy the metal cluster electronically, resulting in unsaturation at the metal centre, and only the smallest molecule, H_2 , is allowed access to the metal centre. Accordingly, for the monodentate phosphite species **2d** and **2e** that show less shielding of the metal centres, hydrogen addition is reversible on application of vacuum.^[27] Iridium dimers, with stronger M–H bonds, are stable with four hydrides, e.g. $L_2Ir_2(\mu-H)_3H$ $L = (C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (“dfepe”) (**3**), but reversibly take up an extra equivalent of H_2 to afford $[(dfepe)Ir(H)_2(\mu-H)]_2$ (**4**), which has two terminal and one bridging hydride ligands per metal centre. The H_2 is lost rapidly when the H_2 atmosphere is removed to regenerate **3**.^[28]

Addition of H_2 to 30-electron $Ir_2(tBu_2PH)_2(CO)_2(H)(\mu-PiBu_2)$ (**5**) results in the generation of the 32-electron dimetallic complex $Ir_2(tBu_2PH)_2(CO)_2(H)_3(\mu-PiBu_2)$ (**6**), in which two hydrides bridge the Ir–Ir connectivity. T_1 values from NMR spectroscopy indicated a dihydride, rather than a dihydrogen, structure. This addition is reversible, both in solution and in the solid state, and **6** loses H_2 when placed under vacuum or exposed to a N_2 purge.^[29] The unsaturated, thiol-bridged bimetallic rhodium complex $[Rh(\text{triphos})(\mu-S)]_2[BPh_4]_2$ (**7**) [triphos = $MeC(CH_2)PPh_2_3$] reacts with H_2 to give $[Rh(\text{triphos})H(\mu-SH)]_2[BPh_4]_2$ (**8**), in which H_2 has undergone heterolytic H_2 cleavage^[30] to form a Rh-hydride and a $\{\mu-SH\}$ group, presumably via a coordinated dihydrogen intermediate. Removing the H_2 under a stream of argon regenerates **7**.^[31] Although a dihydrogen intermediate has not been isolated, NMR spectroscopic studies indicate stepwise addition of H_2 , sequentially at each Rh centre. DFT calculations support this, with a calculated barrier to reversible H_2 loss of $35.1 \text{ kcal mol}^{-1}$.^[32] These complexes also model the reversible, heterolytic cleavage of H_2 in hydrogenase enzymes.

Reversible H_2 gain and loss is reported for the heterometallic, 58-electron, formally unsaturated cluster, $Os_3Pt(\mu-H)_2(CO)_{10}(PCy_3)$ (**9**), which adds H_2 at high pressure (200 atm) to give the electron-precise, 60-electron cluster $Os_3Pt(\mu-H)_4(CO)_{10}(PCy_3)$ (**10**). Purging with N_2 reforms the starting material.^[33]



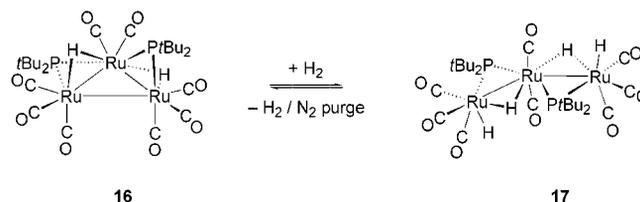


Duckett, Dyson and Johnson have reported the reversible addition of H₂ to a triruthenium cluster Ru₃(CO)₁₀(PMe₂Ph)₂ (**11**), which gives a mixture of two exchanging isomers of the product of H₂ addition, both of which have a terminal and a bridging hydride (e.g. **12**). On removal of the H₂ atmosphere these complexes disappear, suggesting that the H₂ binding is reversible. Varying the H₂ concentration affords thermochemical data for this process and shows that an equilibrium is established for H₂ addition. Interestingly, the mechanism of H₂ addition, as well as the exchange of the isomers, invokes a heterolysis of a Ru–Ru bond and an η²-H₂ ligand bound at a coordinatively unsaturated Ru centre.^[34] Reversible addition of H₂ to ruthenium carbonyl clusters, Ru₃H(μ-COMe)(CO)₁₀ (**13**) by displacement of CO to form Ru₃H₃(μ-COMe)(CO)₁₀ (**14**) has been reported by Keister. Kinetic experiments suggest that the rate-determining step is oxidative addition of H₂ at one of the metal centres after CO loss.^[35] Reversible addition of H₂/CO (at 6.2 bar, 60 °C) to the Rh^I complex *rac*-[Rh₂(CO)₄(L)][BF₄]₂, which does not have a Rh–Rh bond, affords the spectroscopically characterised [Rh^{II}]₂ dimer *rac*-[Rh₂H₂(μ-CO)₂(CO)₂(L)][BF₄]₂ [L = (Et₂PCH₂CH₂)P(Ph)CH₂P(Ph)CH₂CH₂PEt₂].^[36]

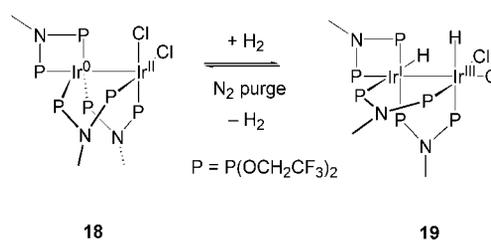
Platinum- and palladium-gold clusters such as [Pt(AuPPh₃)₈][NO₃]₂ (**15**) have been shown to be excellent catalysts for H₂/D₂ equilibration to form HD. The mechanism proposed invokes reversible addition of both H₂ and D₂ to the metal cluster to afford metal hydride species,^[37] which have been observed experimentally to form reversibly on addition of H₂.^[38] A theoretical analysis suggests that activation occurs at the platinum centre, with dihydrogen and dihydride tautomers being close in energy – consistent with the rapid HD exchange observed experimentally.^[39] The unsaturated, 46-electron triosmium dihydride cluster Os₃(CO)₁₀(μ-H)₂ similarly catalyses H₂/D₂ equilibration, but the presumed saturated intermediate HOs₃(CO)₁₀(μ-H)(η²-H₂) has never been isolated or spectroscopically observed.^[40] Computational studies have demonstrated that the H/D exchange mechanism in the binuclear polyhydride complex Cp*Ru(μ-H)₄RuCp*^[41] on addition of D₂ proceeds by an associative mechanism via a number of η²-H₂, η²-HD and η²-D₂ intermediates that are not experimentally observed.^[14]

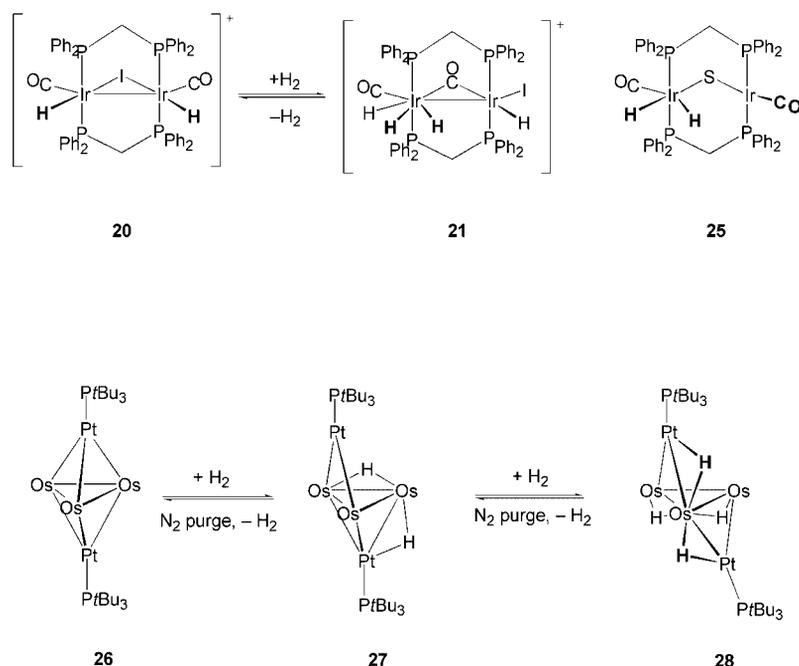
H₂ addition to the saturated 48-electron triangular cluster (μ-H)₂Ru₃(CO)₈(μ-PtBu₂)₂ (**16**) results in the opening up of the cluster to form a linear, also electron-precise, Ru₃ trimetallic species (μ-H)₂Ru₃(CO)₈(μ-PtBu₂)₂ (**17**), with no overall loss of CO. Purging a solution with N₂ reforms

the starting cluster **16**, although in the solid state the cluster is stable to H₂ loss.^[42] Detailed kinetic studies demonstrated that the mechanism involves CO loss (thus forming an unsaturated cluster) that precedes H₂ addition to a single-metal centre with concomitant breaking of a Ru–Ru bond. Addition of CO affords the product that has made a net gain of H₂. Interestingly, this reaction does not occur with other bridging phosphido complexes (such a PPh₂ or PCy₂), and steric arguments are invoked that involve weakening of the Ru–Ru bonding and promotion of CO loss by the bulky PtBu₂ groups.^[43] Hydrogen addition is suggested to occur at the unsaturated metal centre and not across a metal–metal bond, consistent with orbital symmetry arguments.^[44]



Nocera has reported that the mixed-valence, unsaturated, 32-electron, Ir₂ dimer **18** reversibly adds H₂ across the Ir–Ir bond to form saturated dihydride **19**.^[45] Purging with N₂ recovers **18**. The mechanism is suggested to proceed by addition of H₂ to one metal centre and then hydride migration rather than the symmetry-forbidden concerted 1,2 addition. Subsequent DFT calculations support this mechanism and show that addition of H₂ occurs at one metal centre (to give a dihydrogen complex) and passes through a transition structure with a terminal and bridging hydride, finally to rest at a terminal hydride on each Ir centre.^[46] Interestingly, experimentally the reversible hydrogen addition is solvent-dependant. Removal of the H₂ atmosphere from a CH₂Cl₂ solution of **19** regenerates **18**, but in CH₃CN solutions the solvent has to be evaporated for H₂ loss to occur. It is suggested, from crystallographic evidence, that H-bonding interactions with acetonitrile impose a kinetic barrier to H₂ loss.





carbonyl groups not shown for clarity

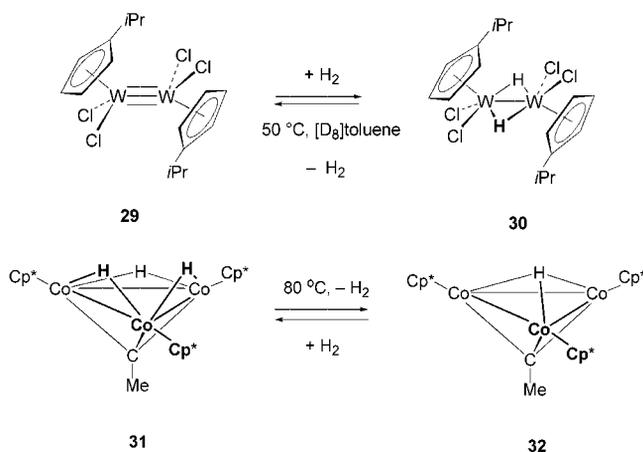
Cowie and Vaartstra reported that addition of H₂ to the A-frame iridium dimer, [Ir₂(dppm)₂H₂(CO)₂I][BF₄] (**20**), gives the fluxional tetrahydride, [Ir₂(dppm)₂H₄(CO)₂I][BF₄] (**21**), for which *T*₁ measurements indicate that all the metal-bound hydrogen ligands are hydride-like. Removing the H₂ atmosphere regenerates **20** on gentle warming. The neutral, diiodido complex Ir₂(dppm)₂(CO)₂I₂ (**22**) also reversibly adds H₂ to give a dihydride, Ir₂H₂(dppm)₂(CO)₂I₂ (**23**), which loses H₂ upon being purged with N₂.^[47] Although **20** is a 34-electron cluster, and thus would not be expected to add further H₂ without rupturing the Ir–Ir bond, the bridging iodine moves to a terminal position in the product **21** (3 e[−] to 1 e[−]), allowing for overall H₂ addition. Duckett and co-workers have studied a related compound, Ir₂(dppm)₂(CO)₂(μ-S)₂ (**24**), by using parahydrogen-induced polarisation NMR spectroscopy, and they also showed that the product of addition of H₂, Ir₂(dppm)₂(CO)₂(H)₂(μ-S)₂ (**25**), also loses H₂ upon being purged with N₂.^[48] In this case, H₂ addition transforms a square planar Ir^I centre into an octahedral Ir^{III} centre.

Trigonal bipyramidal, 68-electron Pt₂Os₃(CO)₁₀(PtBu₃)₂ (**26**) takes up two molecules of H₂ reversibly in a stepwise manner to eventually give Pt₂Os₃(CO)₁₀(PtBu₃)₂H₄ (**28**) through the (isolated) intermediate **27**. Purging with N₂ removes the bound H₂ to reform **26**, although this reaction only gives 28% of the starting material back. The low reverse-conversion is attributed to the open structure of **28** that is more prone to decomposition. On addition of H₂, **26** undergoes successive Os–Pt cleavages to give an Os₃ triangle with two edge bridging {Pt(CO)PtBu₃} groups. This behaviour is in contrast to other, closely related, clusters

such as **40** and **41** in which addition of H₂ results in no significant core cluster change.^[49]

Thermally Reversible or Reversible When Placed Under Vacuum

Oxidative addition of H₂ to the formal triple bond of [(η⁵-C₅H₄iPr)WCl₂]₂ (**29**) gives complex **30**, [(η⁵-C₅H₄iPr)W(μ-H)Cl₂]₂, which has bridging dihydrides clearly identified by using NMR spectroscopy by very long *T*₁ times of approximately 1.2 seconds. Gentle heating of **30** results in the reversible (quantitative by NMR spectroscopy) loss of H₂ to reform **29**.^[50]



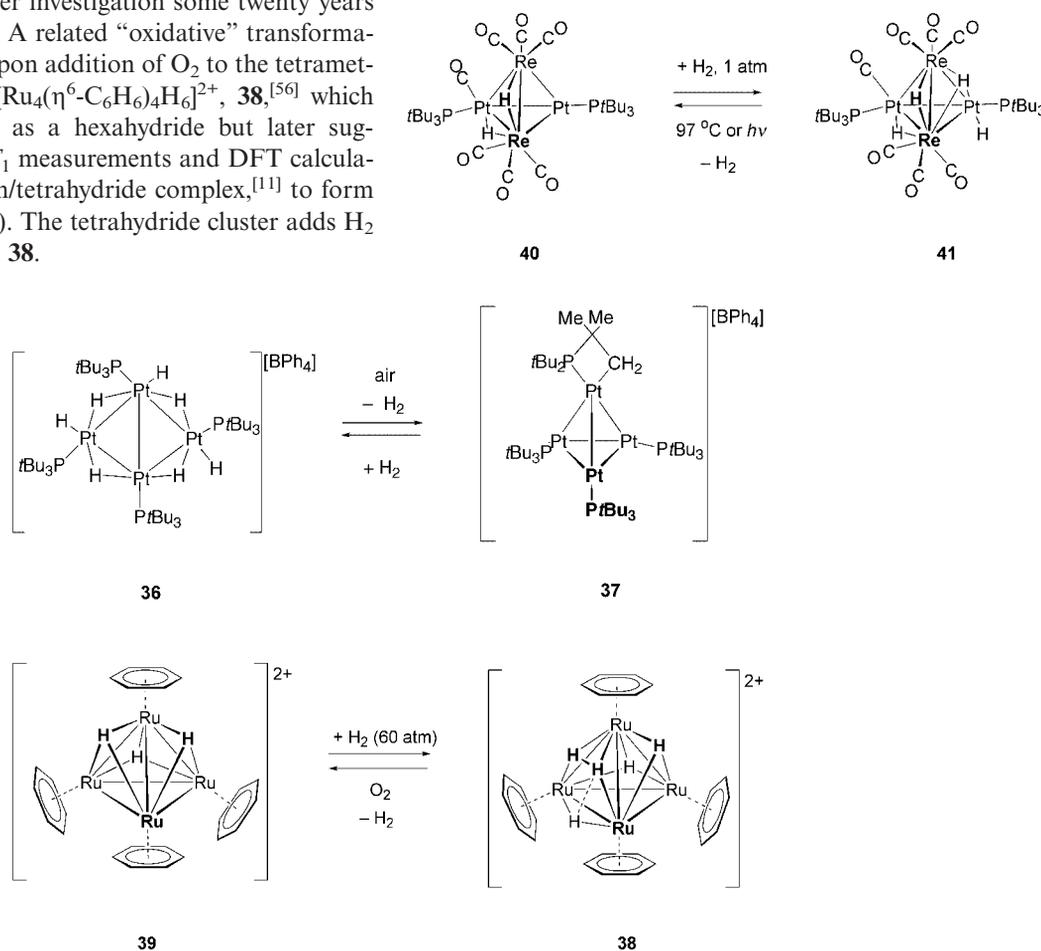
The 48-electron, cluster (Cp*Co)₃(μ₂-H)₃(μ₃-CMe) (**31**) reversibly loses H₂ when heated to 80 °C, to afford the para-

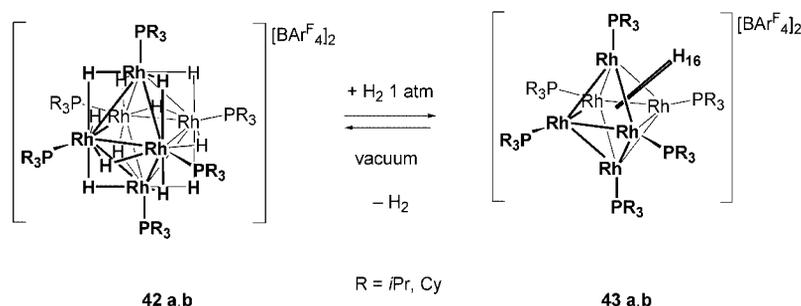
magnetic, 46-electron cluster $(\text{Cp}^*\text{Co})_3(\mu_3\text{-H})(\mu_3\text{-CMe})$ (**32**). ΔG^\ddagger for this process is calculated as $23.8 \text{ kcal mol}^{-1}$.^[51] Related chemistry involving reversible addition of H_2 to the unsaturated cluster $\text{Cp}^*_3\text{Co}_3(\mu_3\text{-CO})_2$ (**33**) yields similar activation parameters.^[52] The valence isoelectronic clusters $\text{Cp}^*_3\text{Rh}_2\text{M}(\mu_3\text{-CO})_2$ (**34**) ($\text{M} = \text{Co}, \text{Ir}$) also add H_2 reversibly to form $\text{Cp}_3\text{Rh}_2\text{M}(\mu_3\text{-CO})_2(\mu\text{-H})_2$ (**35**). Warming (to an unspecified temperature, $\text{M} = \text{Rh}$) releases the H_2 to reform the unsaturated trimetallic cluster.^[53]

The 56-electron platinum cluster $[\text{Pt}_4\text{H}_7(\text{PtBu}_3)_4][\text{BPh}_4]$ (**36**), reported by Spencer in 1984, loses H_2 by “atmospheric oxidation” to afford the C–H activated complex $[\text{Pt}_4(\text{PtBu}_3)_3\{\text{PtBu}_2(\text{CMe}_2\text{CH}_2)\}][\text{BPh}_4]$ (**37**), which formally has 50 electrons (this complex was not crystallographically characterised). Cluster **36** can be regenerated by adding H_2 (1 atm, 293 K) to **37**.^[54] The conversion of **36** to **37** represents a remarkable net loss of 8 hydrogen atoms. Again, the bulky *tert*-butyl groups on the phosphanes no doubt stabilise the cluster towards H_2 loss. Although this transformation is described as an oxidation, it might also better be described as initial stepwise loss of 3H_2 , oxidative addition of C–H and loss of H_2 . Interestingly, the isoelectronic *neutral* cluster $\text{Pt}_4\text{H}_8(\text{PtBu}_3)_4$ is not reported to lose H_2 ,^[55] but whether this is a simple consequence of the fact that this complex was never left on the open bench is not clear! Whatever the reason, these unsaturated platinum complexes are fascinating, given the reversible addition of a large amount of H_2 , and surely warrant further investigation some twenty years after they were reported. A related “oxidative” transformation to **36** \rightarrow **37** occurs upon addition of O_2 to the tetrametallic ruthenium cluster $[\text{Ru}_4(\eta^6\text{-C}_6\text{H}_6)_4\text{H}_6]^{2+}$, **38**,^[56] which initially was formulated as a hexahydride but later suggested (on the basis of T_1 measurements and DFT calculations) to be a dihydrogen/tetrahydride complex,^[11] to form $[\text{Ru}_4(\eta^6\text{-C}_6\text{H}_6)_4\text{H}_4]^{2+}$ (**39**). The tetrahydride cluster adds H_2 again (60 atm) to reform **38**.

Adams and co-workers have recently reported a set of unsaturated platinum-rhenium complexes with bulky *t*Bu₃P ligands that allow for electronically unsaturated clusters to be synthesised in a systematic manner. $\text{Pt}_2\text{Re}_2(\text{CO})_7(\text{PtBu}_3)_2\text{-H}_2$ (**40**), an unsaturated 54-electron tetrahedral cluster (tetrahedral Pt_2M_2 often have an electron count of 58, especially when decorated with bulky ligands, e.g. $\text{Pt}_2\text{Mo}_2(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{CO})_6(\text{PCy}_3)_2$ ^[57]), takes up H_2 to form $\text{Pt}_2\text{Re}_2(\text{CO})_7(\text{PtBu}_3)_2\text{H}_4$ (**41**), which has 4 hydride ligands. Cluster **41** eliminates H_2 nearly quantitatively on heating to 97°C or on irradiation (UV/Vis). The mechanism for H_2 addition (and by the principle of microscopic reversibility, that for H_2 loss) has been studied by DFT methods and involves end-on η^1 -attack of H_2 on one of the Pt atoms (where the LUMO is centred), moving through an $\eta^2\text{-H}_2$ intermediate, which oxidatively adds to the same Pt atom to give the observed product.^[58] Addition of hydrogen results in no gross structural change to the cluster (i.e. metal–metal bond scission or rearrangement of the polyhedral core), consistent with the addition of electron pairs to an unsaturated cluster.

The clusters $[\text{Rh}_6(\text{PR}_3)_6\text{H}_{12}][\text{BAR}^F_4]_2$ (**42**) ($\text{R} = i\text{Pr}$ **42a**, Cy **42b**) reversibly take up two equivalents of H_2 to give the sixteen-hydride clusters $[\text{Rh}_6(\text{PR}_3)_6\text{H}_{16}][\text{BAR}^F_4]_2$ (**43a,b**).^[59] This uptake is rapid (less than 5 min). Placing **43a** or **43b**





under vacuum removes the H_2 and regenerates **42a,b**, both in solution and the solid state. As for **40**, these clusters can be considered as being unsaturated (76-electrons) and DFT calculations show that there are two low-lying empty orbitals available for the take-up of two H_2 bonding pairs.^[60] Again, it is the bulky alkylphosphane ligands that shield the metal core from decomposition and allow the low electron count to be maintained. DFT calculations also indicate that the sixteen-hydride cluster contains an interstitial hydride and two dihydrogen-like H_2 molecules, which have an average binding energy to the cluster of 60 kJ mol^{-1} , consis-

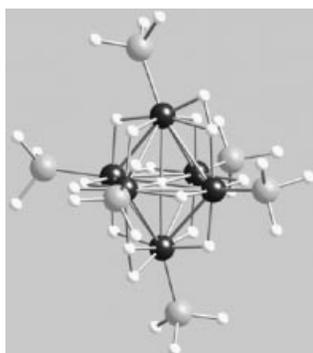
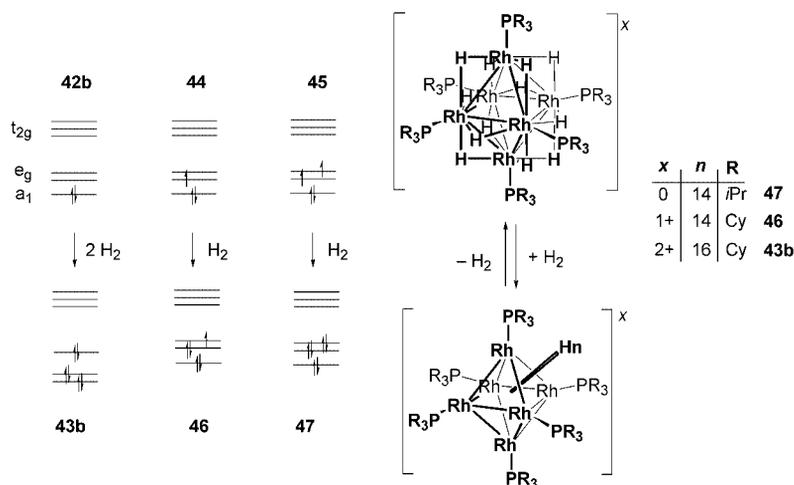


Figure 4. The DFT calculated structure of $[\text{Rh}_6(\text{PH}_3)_6\text{H}_{16}]^{2+}$, showing the two dihydrogen-like ligands.

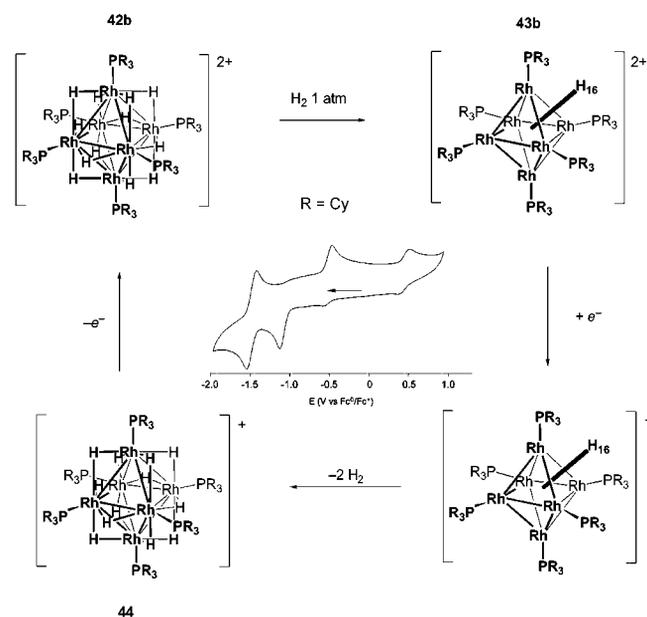
tent with that reported for mononuclear dihydrogen complexes (Figure 4).^[5] Although these dihydrogen ligands are not observed either by X-ray crystallography or NMR spectroscopy, indirect evidence comes from H/D exchange experiments with D_2 and the observation of $\text{HD}(\text{g})$. The reversible H_2 loss can be modulated by the phosphane. With $\text{P}i\text{Pr}_3$, H_2 loss from **43a** when placed under vacuum is relatively quick (12 hours), but for **43b** with PCy_3 ligands, H_2 loss under vacuum takes 1 week. This difference is accounted for by the tighter interdigitation of the cyclohexyl groups that kinetically stabilise the cluster towards H_2 loss.

Reduction of clusters **42** affords $[\text{Rh}_6(\text{PR}_3)_6\text{H}_{12}]^{n+}$ ($n = 1$ **44**, 0 **45**).^[61] Inspection of the frontier molecular orbitals suggests that these clusters should also take up one equivalent of H_2 . The cluster $[\text{Rh}_6(\text{PR}_3)_6\text{H}_{12}]^+$ (**44**) adds one H_2 to give $[\text{Rh}_6(\text{PR}_3)_6\text{H}_{14}]^+$ (**46**), as characterised by ESI-MS. Removing the H_2 atmosphere regenerates **44**. By contrast, neutral $[\text{Rh}_6(\text{PR}_3)_6\text{H}_{12}]$ (**45**), which is a paramagnetic species having a triplet ground state ($S = 1$), takes up H_2 to give the diamagnetic cluster $[\text{Rh}_6(\text{PR}_3)_6\text{H}_{14}]$ (**47**) ($S = 0$, $\text{R} = i\text{Pr}$ only). This reaction is much slower than for the other clusters (16 hours), attributed to “spin blocking” – a significant barrier along the reaction coordinate induced by a spin change that results in a significantly slower reaction when there is a spin-state change.^[62] Consistent with microscopic reversibility arguments, **45** does not lose H_2 readily.



Electrochemically Reversible

Inspection of the MO diagram for **43a,b** suggests that addition of one extra electron would result in the population of a high-lying orbital, and this could destabilise the cluster, resulting in H₂ loss to re-establish a large HOMO–LUMO gap. If coupled with a sequential oxidation of the cluster, this potentially could lead to the reversible binding and release of H₂, triggered by a single-electron redox event. This prediction was borne out experimentally.^[60,61,63] The cyclic voltammogram of **43b** shows an irreversible loss of H₂ on reduction, presumably from an unstable, putative species [Rh₆(PCy₃)₆H₁₆]⁺ (Scheme 3). The formation of [Rh₆(PCy₃)₆H₁₂]⁺ (**44**) results, which can be oxidised to form [Rh₆(PCy₃)₆H₁₂]²⁺ (**42b**) and subsequently recharged with H₂ to reform [Rh₆(PCy₃)₆H₁₆]²⁺ (**43b**), completing a complete hydrogen-store cycle. The loss of H₂ is kinetically fast (*t*_{1/2} as measured electrochemically is 170 ms). The redox cycle can be duplicated by using chemical reductants/oxidants and followed by ESI-MS. This facile, reusable gain and loss of two equivalents of H₂ by using a simple one-electron redox switch represents a new method of hydrogen storage. Although the overall storage capacity is very low (0.1% by weight), the attractive conditions of room temperature and pressure, actuation by the addition of a single electron and rapid desorption kinetics makes the concept of interest for future H₂ storage applications.



Scheme 3. Insert shows the cyclic voltammogram; the irreversible reductions are attributed to H₂ loss at ≈ 1.0 V.

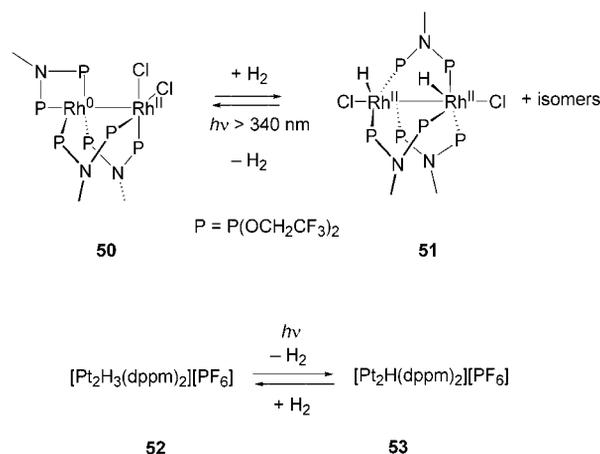
Redox-induced loss of hydrogen or protons is known to occur in mononuclear systems. Irreversible oxidation of the complex [Co{P(CH₂CH₂PPh₂)₃}(H₂)] [PF₆]^[64] (originally suggested to be a dihydrogen complex, but later reformulated by Heinekey as a dihydride^[65]) results in the loss of a proton, while reduction of vinylidene complex [Rh(=C=CHPh){N(CH₂CH₂PPh₂)₃][BF₄] results in H₂ loss, to form an acetylide.^[66] Redox-promoted oxidation of

H₂ to afford protons (or the reverse reaction – electrocatalytic generation of H₂) is, of course, also very well documented in the study of hydrogenase chemistry.^[67] However, none of these processes involves the reversible binding of H₂ as found for **43b**.

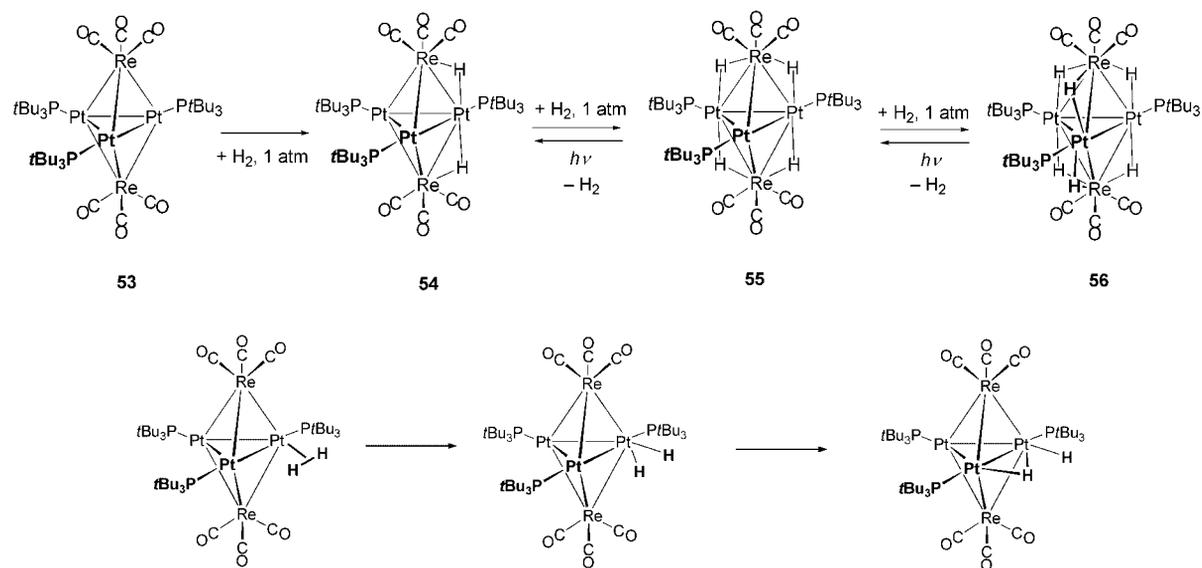
Photochemically Reversible

An early (1983) report of the photolysis of (η⁵-C₅H₅)W(CO)₃H suggested that it proceeded by CO/H₂ expulsion to afford a putative dimeric species [(η⁵-C₅H₅)W(CO)₂]₂ (**48**) that reversibly added H₂ under photochemical conditions to give [(η⁵-C₅H₅)W(μ-H)(CO)₂]₂, (**49**), which is related to **30**.^[68] Aspects of the dimerisation mechanism have been subsequently questioned.^[69]

The rhodium analogue of **19**, complex **51**, can be formed by addition of H₂ to **50**. Interestingly, complex **51** does not lose H₂ readily on standing, nor does it exchange with D₂ appreciably after one week. However, H₂ loss is fast upon photochemical irradiation to afford **50**.^[70] These complexes provide insight into the photocycle for hydrogen production from HX solutions. [Pt₂H₃(dppm)₂][PF₆] (**52**) loses H₂ in solution and the solid state on irradiation to give a complex of formula [Pt₂H(dppm)₂][PF₆] (**53**), which reacts back slowly with H₂ to give **52**.^[71]



The electronically unsaturated, 62-electron trigonal bipyramidal cluster Pt₃Re₂(PtBu₃)₃(CO)₆ (**53**) adds three molecules of H₂ in a stepwise manner to eventually afford Pt₃Re₂(PtBu₃)₃(CO)₆H₆ (**56**). This reaction is reversible under photolytic conditions, and irradiating **56** eliminates dihydrogen, ultimately to afford the dihydride complex Pt₃Re₂(PtBu₃)₃(CO)₆H₂ (**54**). The last elimination of H₂ is presumably a high-energy process and does not occur under the conditions used.^[72] Cluster **53** is unsaturated by 10 electrons for a trigonal bipyramid (albeit platinum clusters often count lower than expected), and the bulky *t*Bu₃P groups no doubt have a role to play in this – stabilising the unsaturated core by providing a steric shield against addition of further, large, metal fragments. Space-filling diagrams nonetheless indicate that there is sufficient room for the approach of a H₂ molecule. The molecular orbital structure shows five low-lying unoccupied molecular orbitals,

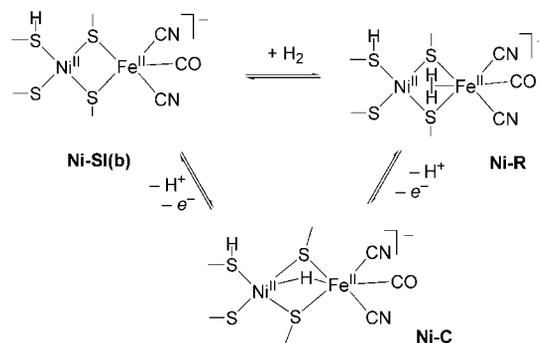


Scheme 4.

three of which are suitably aligned along the Pt–Re bonds to accept electron density from an incoming H_2 molecule. Detailed theoretical analysis of the mechanism of H_2 addition indicates a possible pathway that starts with hydrogen addition at Pt to give a dihydrogen intermediate, followed by H_2 cleavage and the formation of a complex with a terminal hydride and a hydride bridging a Pt–Pt bond. This configuration rearranges to give the observed product with hydrides bridging the Pt–Re bonds (Scheme 4). The related tetranuclear cluster $\text{Pt}_2\text{Re}_2(\text{CO})_7(\text{tBu}_3\text{P})_2\text{H}_4$ (**41**) also eliminates one equivalent of H_2 on irradiation.^[58,73] The addition of H_2 to a single metal centre is consistent with qualitative molecular orbital arguments by Hoffman, who showed that intramolecular reductive elimination (and the microscopic reverse: oxidative addition) would be symmetry-forbidden for 1,2-elimination (or 1,2-addition) and have a large barrier for a concerted least-motion pathway.^[44]

Reversible Biological Systems

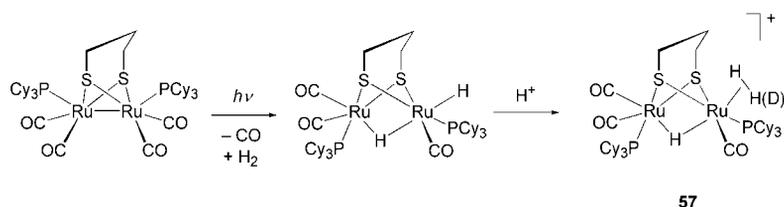
Hydrogenases regulate the metabolism of hydrogen in microorganisms, and these enzymes have attracted an enormous amount of attention in the hope of developing electrochemically active, bio-inspired catalytic systems employing hydrogen.^[74] The active site of one class of these enzymes have been shown crystallographically to contain a dinuclear NiFe cluster with bridging sulfur ligands. The reversible binding of hydrogen at the active site is a key stage in the proposed mechanism of action, and the presence of the biologically unusual, strong-*trans*-influence CO ligand favours this process (by reducing the ability of the metal to back-donate into the σ^* orbital of H_2). Heterolytic cleavage of H_2 follows the binding event, generating a bridging hydride ligand and releasing a proton. The salient part of the enzymatic cycle is shown in Scheme 5.



Scheme 5.

Ni-SI(b) (the mechanism has its own shorthand) reacts with H_2 to generate **Ni-R**, in which the hydrogen is suggested to be present as a dihydrogen ligand bound to Fe^{II} . One-electron oxidation of **Ni-R** liberates a proton to generate **Ni-C**, thought to possess a bridging hydride ligand, which, upon further one-electron oxidation, is released as a proton, and **Ni-SI(b)** is regenerated. The involvement of the hydride and dihydrogen intermediates is implicated by the fact that during catalyst turnover under a D_2 atmosphere, HD and/or HDO is formed, despite the lack of spectroscopic evidence for the existence of metal–hydride or metal–dihydrogen species. Catalysis of H/D exchange reactions is characteristic of the hydrogenases.^[75]

Iron-only hydrogenases also exist, containing a $\{\text{Fe}_4\text{S}_4\}$ cubane cluster linked to a $\{\text{Fe}_2\text{S}_3\}$ subsite through a bridging cysteinyl ligand. The fact that both the NiFe and Fe_2 units have thiolate, CN^- and CO ligands – all common in coordination chemistry – means that a huge range of dinuclear complexes have been synthesised with the aim of modelling the geometry, connectivity, metals, ligand sets and chemistry displayed by the hydrogenases.^[76] This topic has



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been heavily reviewed, so only a few examples with particular relevance to reversible hydrogen binding will be mentioned herein.

Many complexes designed to model the hydrogenases react *irreversibly* with H₂, such as the recent example of a water-soluble NiRu complex that takes up H₂ under ambient conditions, resulting in heterolytic cleavage of H₂ to form H⁺ and a bridging hydride.^[77] Less common are dinuclear complexes that react reversibly with hydrogen; a notable example is from Rauchfuss, who characterised the first dihydrogen complex of a hydrogenase active site model.^[78]

[Ru₂(μ-H)(H₂)(μ-SCH₂CH₂CH₂S)(PCy₃)₂(CO)₃]⁺ (**57**) was shown to catalyse H₂/D₂ equilibration. Related complexes also catalyse H/D scrambling via what is assumed to be an (η²-H₂)-containing intermediate; examples of compounds displaying this chemistry include [Fe₂(μ-H)(μ-SCH₂CH₂CH₂S)(PMe₃)₂(CO)₄]⁺ (**58**)^[79] and [Fe₂(μ-H)(μ-SCH₂CH₂CH₂S)(CN*t*Bu)₂(CO)₄]⁺ (**59**).^[80] A vacant coordination site must first be created, and, consistent with this requirement, the H/D scrambling reaction is often promoted by irradiation with UV light but inhibited by the presence of CO.

Giant Clusters Displaying Reversible H₂ Binding

Palladium metal has an unusually high affinity for hydrogen, absorbing up to 935 times its own volume (an approximate composition of Pd₄H₃), and Pd/Ag membranes are used on an industrial scale to produce ultrapure hydrogen.^[81] Various models of the hydrogen-rich lattice have been reported, most notably Dahl's cluster H₁₂Pd₂₈(PtPMe₃)(PtPPh₃)₁₂(CO)₂₇ (**60**) (Figure 5).^[82] The cluster was treated with D₂, which resulted in an 80% decrease in the hydride signal by ¹H NMR spectroscopy, suggesting that hydrogen is readily exchanged. However, no attempt seems to have been made to add H₂ under pressure or to remove it by vacuum, heat or light, so regrettably little is known about the hydrogen storage capabilities of this material.

Giant, ligand-stabilised palladium clusters can be readily synthesised by reduction of palladium acetate with hydrogen gas.^[83] With careful control of conditions, the size distribution is nearly monodisperse (see Figure 6) and centred on particular "magic numbers" corresponding to different numbers of concentric shells (*n*) of Pd atoms around a central atom, where each shell contains (10*n*² + 2) atoms.^[84]

The behaviour of the series Pd₅₅(phen)₃₆O₃₀ (2 shells, diameter ≈ 1 nm; phen = phenanthroline), Pd₅₆₁(phen)₃₆O₂₀₀ (5 shells, diameter ≈ 2.6 nm), Pd₁₄₁₅(phen)₆₀O₁₁₀₀ (7 shells, diameter ≈ 3.7 nm) and Pd powder (diameter ≈ 50 μm) towards hydrogen has been investigated in detail by

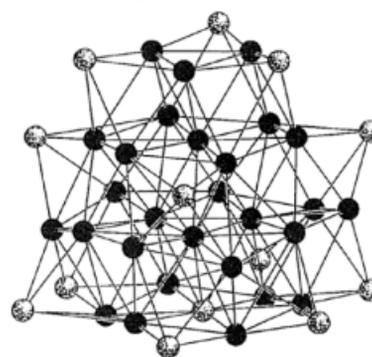


Figure 5. Crystallographically determined metal core (Pd black, Pt grey) structure of H₁₂Pd₂₈(PtPMe₃)(PtPPh₃)₁₂(CO)₂₇ (**60**). Hydrogen atoms were not located. Figure reproduced courtesy of the American Chemical Society from ref.^[83]

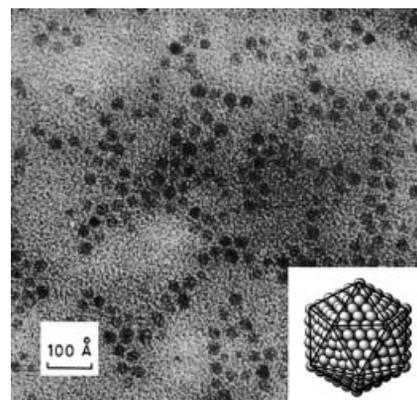


Figure 6. Electron micrograph of palladium nanoparticles deposited on a carbon support. Reproduced courtesy of the Royal Society of Chemistry from ref.^[84] Inset: idealised icosahedral structure of Pd₅₆₁ core, approximate diameter 26 Å.

Züttel and co-workers. They found that Pd clusters of all size ranges reversibly absorbed and desorbed hydrogen,^[85] but that the reversible hydrogen storage capacity (H/Pd ratio) decreased with decreasing cluster size.^[86] This effect was attributed to the fact that the smaller clusters had a greater proportion of surface atoms and that only the interstitial sites in the Pd lattice were available for reversible hydrogen storage. The reasoning here was that the binding energy of the surface hydrides was greater than the interstitial hydrogen, and the surface hydrides could therefore not be easily removed simply by application of vacuum. The cluster samples had dramatically improved discharge kinetics relative to bulk Pd, and X-ray diffraction revealed that the crystallographic structure of the clusters was not altered by absorption and desorption cycles.^[87] However, others have shown that 5-nm Pd clusters do undergo structural change

upon hydrogen absorption, probably from a cubic lattice to an icosahedral one.^[88]

Pd clusters loaded on carbon have been shown to absorb more hydrogen per Pd atom than does bulk Pd,^[89] an effect attributed to spillover (a process whereby hydrogen spreads from a metal particle to its support).^[90] The absorption was shown to be reversible but a significant fraction of the stored hydrogen required pressures of less than 5 Torr or high temperatures in order to be released.

Conclusions

Multimetallic compounds that reversibly bind hydrogen without experiencing dramatic structural changes have several features in common:

(i) Bulky ligands (especially phosphanes) are often a feature of the coordination sphere. Such ligands provide kinetically controlled steric blocking of coordination sites, favouring electronic unsaturation. However the smallest of molecules, H₂, is often able to penetrate the coordination sphere and binds to the metal to (sometimes only partially) relieve the electronic unsaturation at the metal centre.

(ii) The metals involved are generally late-transition metals, especially Rh, Pd and the surrounding elements, in relatively low oxidation states. Such metals form strong bonds with soft ligands such as the bulky phosphanes that appear to be crucial for successful reversible hydrogen bonding; they also have sufficient d electrons for back-donation to the σ^* orbital on H as well as suitable empty acceptor orbitals.

(iii) The hydrogen does not have to be bound side-on as η^2 -H₂ in order for reversible binding behaviour to be observed; the rapid exchange between the wide variety of binding modes (including bridging and interstitial) and the low energy differences between them facilitates the ready distribution of H ligands around the cluster core (hence making definitive characterisation of H location often problematic).

Approaches to multimetallic complexes that reversibly bind hydrogen have historically resulted from serendipity as much as from an avowed intention to make compounds with this useful and interesting property (with the notable exception of the efforts to model the hydrogenases). However, a few simple design rules outlined above seem to apply quite generally and it is reasonable to expect that the field will develop by further exploitation of the structural variety and rich redox properties offered by polynuclear metal cores and the kinetic blocking of coordination sites by bulky ligands. Firm establishment of the structure–property relationships inherent to systems that efficiently and reversibly bind hydrogen should allow the application of these concepts to other (cheaper!) metals and materials.

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