

The multifarious world of transition metal hydrides

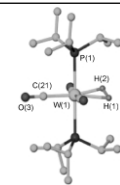
G. Sean McGrady^{*a} and Gemma Guilera^b

^a Department of Chemistry, University of New Brunswick, Fredericton, N.B., Canada E3B 6E2

^b Department of Chemistry, King's College London, Strand, UK WC2R 2LS

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Transition metal (TM) hydrides display a remarkable range of bonding types, encompassing classical M–H moieties, dihydrogen complexes containing the η^2 -H₂ ligand, and trihydrides which display quantum mechanical site exchange. Furthermore, C–H, Si–H and B–H moieties can bind to TM centres in an η^2 -manner, to give σ -bond complexes with a spectrum of M...H contributions. In addition to these primary bonding modes, TM complexes also indulge in a wide spectrum of hydrogen-bonding interactions, including both M...H–X and the unique type M–H...H–X. This review begins with a historical perspective of the development of TM hydride chemistry, and proceeds to focus on three significant developments of the past two decades: the discovery of σ -bond and dihydrogen complexes, the involvement of TM hydrides in hydrogen bonding, and the role played by quantum mechanical phenomena in the chemistry and dynamics of TM hydrides. The account concludes with an overview of the inter-relationship between these apparently disparate novel aspects of TM hydride chemistry.

1 Introduction

With but a single 1s valence orbital, the chemistry of hydrogen may be expected to be rather simple. That it is anything but is a

testament to this same electronic simplicity. For the absence of core and non-bonding valence electrons, remarkably good overlap with the valence orbitals of many other elements, and an anomalously high electronegativity endow the H–X moiety with a particularly rich and diverse chemistry, including an unparalleled capacity to partake in strong intermolecular interactions. In addition, the uniquely small mass of the hydrogen atom allows in many instances for quantum mechanical effects to permeate its chemical behaviour. This review commences with a brief survey of the classical chemistry of TM hydrides, and proceeds to introduce some novel and unique types of complex chemical behaviour which have emerged since the 1980s.

1.1 Classical TM hydride complexes

The binary molecular hydrides of the TMs are ill-defined and generally elusive; only recently has significant progress been made regarding their preparation and characterisation by matrix-isolation methods.¹ For the first half of the 20th Century, TM hydride complexes appeared to have a similar status, being considered intrinsically unstable. The preparation by Hieber of [H₂Fe(CO)₄] in 1931 represented a breakthrough in inorganic chemistry: this sub-class of carbonyl hydrides was developed and explored over the next couple of decades, but they remained something of a curiosity.



Sean McGrady carried out his doctoral research with Tony Downs in Oxford, followed by postdoctoral spells with Helge Willner in Hanover and with Oxford Lasers, Ltd. In 1993 he returned to Oxford as a Junior Research Fellow. He was appointed lecturer at King's College London in 1998, and associate professor at the University of New Brunswick in 2003. His research interests centre on the relationship between structure and reactivity in small inorganic molecules, and the application of a range of techniques for investigating this relationship.

Gemma Guilera was born in 1975 in Barcelona, Catalonia. She studied at the University of Barcelona where she received her BSc in Chemistry in 1998. In 1999 she obtained a MSc under an ERASMUS program between University of Barcelona and King's College London. She has recently completed her PhD in organometallic chemistry at King's College London under the supervision of Sean McGrady. Her research interests concern the involvement of transition metal hydride and borohydride complexes in the formation of unconventional types of interactions.

In 1955 Wilkinson prepared $[\text{Cp}_2\text{ReH}]$, the first organometallic TM hydride. The novel and unique spectroscopic properties of the M–H moiety were soon recognised – in particular the characteristic low frequency for the ^1H NMR resonance of the hydride, between 0 and -30 ppm; and the occurrence in the IR spectrum of M–H stretching vibrations in the region $1700\text{--}2300\text{ cm}^{-1}$. The discipline of organometallic chemistry blossomed at an exponential rate over the next two decades.² Significant new types of TM hydride discovered in this period include borohydride complexes such as $[(\text{PPh}_3)(\text{phen})\text{Cu}(\eta^2\text{-BH}_4)]$, in which a boron hydride moiety acts as a ligand to a TM centre; bridging hydrides such as $[(\text{CO})_5\text{W-H-W}(\text{CO})_5]^-$, which are invariably non-linear; interstitial hydrides like $[\text{Co}_6\text{H}(\text{CO})_{15}]^-$, in which the single H atom is located at the centre of a cluster of metal atoms; and a family of polyhydrides such as $[(\text{PPhPr}_2)_3\text{WH}_6]$, which display uniquely high coordination numbers and are highly fluxional.³ These four representative examples are depicted in Fig. 1.

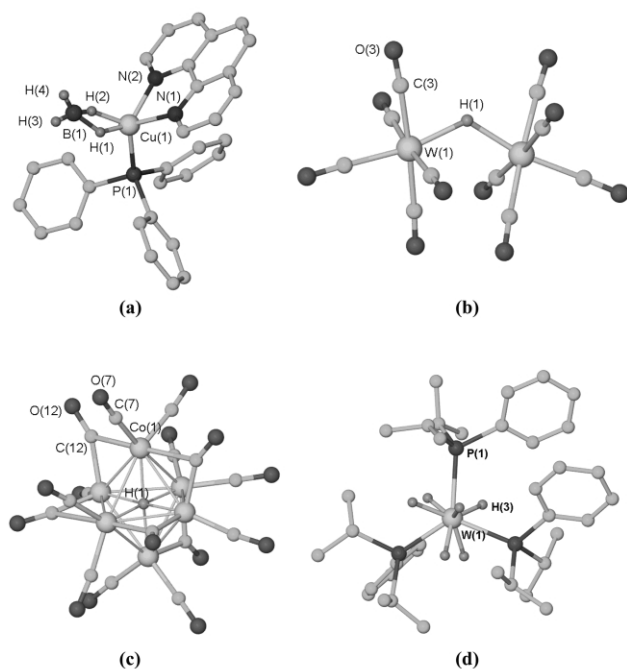


Fig. 1 Molecular structures of (a) $[(\text{PPh}_3)(\text{phen})\text{Cu}(\eta^2\text{-BH}_4)]$, (b) $[(\text{CO})_5\text{W-H-W}(\text{CO})_5]^-$, (c) $[\text{Co}_6\text{H}(\text{CO})_{15}]^-$, and (d) $[(\text{PPhPr}_2)_3\text{WH}_6]$, as determined by neutron diffraction. Redrawn from ref. 3.

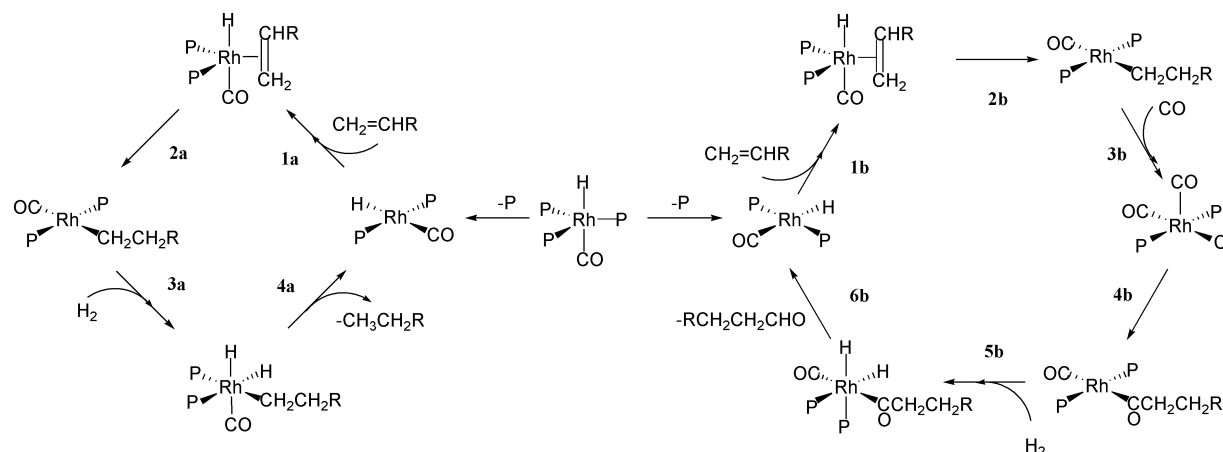
Whilst the characteristic NMR and IR signatures of TM hydrides greatly assist their spectroscopic characterisation, diffraction techniques encounter severe problems. The low

scattering power of hydrogen in the vicinity of a heavy element makes accurate location of hydrides by X-ray diffraction particularly problematic. Until recently, the position of the H atom was often inferred from an apparently vacant coordination site at the metal. Modern instrumentation and software have ameliorated this situation, but the technique of choice for full and accurate structural characterisation of TM hydride complexes remains neutron diffraction. The high cost and low availability associated with this technique, however, mean it can be applied only to a limited number of systems.

1.2 Reactivity of TM hydride complexes

TM hydrides now play a central role in synthetic, structural and catalytic inorganic and organometallic chemistry. Indeed, virtually all the major industrial processes in the petrochemical industry rely on the involvement of an M–H moiety in one or more key step. With negligible steric encumbrance, no non-bonding valence electrons to interfere in its chemistry, and a non-directional valence orbital with good overlap characteristics, the M–H moiety is remarkably labile, taking part in a wide range of migration and insertion reactions at TM centres. Two examples are depicted in Scheme 1 for the versatile system $[(\text{PPh}_3)_3(\text{CO})\text{RhH}]$, which catalyses both alkene hydrogenation and hydroformylation (in the Union Carbide process).² These two different processes share a common intermediate in the electronically and coordinatively unsaturated intermediate $[(\text{PPh}_3)_2\text{Rh}(\text{CO})(\eta^2\text{-CH}_2\text{CHR})]$. In the hydrogenation reaction, oxidative addition of H_2 is followed by reductive elimination of the alkane product. In the hydroformylation reaction, this process also occurs as the final stage, but is preceded by uptake of a molecule of CO which rapidly inserts into the M–alkyl bond, resulting in an aldehyde with one carbon atom more than the starting alkene.

Whilst X-ray and neutron diffraction have provided the most direct structural information about TM hydrides, NMR spectroscopy has proved the mainstay of studies of their reactivity in solution. Many hydride systems are fluxional on the NMR timescale, although extracting detailed information about the exchange mechanism is often less than straightforward. The observation and characterisation of reactive intermediates in catalytic cycles of the type shown in Scheme 1 often presents formidable problems. The inherently low sensitivity of NMR, allied to the low concentrations and short lifetimes of species such as $[(\text{PPh}_3)_2\text{RhH}(\text{CO})(\eta^2\text{-CH}_2\text{CHR})]$ make them very difficult to detect and study by conventional NMR methods. A major advance in this area has been the use of parahydrogen, $p\text{-H}_2$, to explore the structure and reactivity of hydride intermediates.^{4a} Parahydrogen possesses a non-Boltzmann spin population, and this enhances the inherently low sensitivity of



Scheme 1 Cycles showing the stages in catalysis of alkene hydrogenation (left) and hydroformylation (right) by $[(\text{PPh}_3)_3(\text{CO})\text{RhH}]$. In each case, PPh_3 is represented as P.

the NMR experiment by up to several orders of magnitude. For example, the addition of H_2 to *trans*- $[(\text{PPh}_3)_2\text{Ir}(\text{CO})\text{Cl}]$ (Vaska's Complex) is a textbook example of oxidative addition, known to occur by a concerted mechanism which places the hydrides in a mutually *cis* orientation in the six-coordinate product. Use of *p*- H_2 to explore this reaction surprisingly revealed a minor kinetic product, *cis-cis*- $[(\text{PPh}_3)_2\text{Ir}(\text{CO})\text{H}_2\text{Cl}]$, to be formed in addition to the established thermodynamic product *cis-trans*- $[(\text{PPh}_3)_2\text{Ir}(\text{CO})\text{H}_2\text{Cl}]$.^{4b}

2 Non-classical TM hydride complexes

2.1 C–H, Si–H and B–H bonds as ligands: σ -bond complexes

The strength, non-polar nature and tightly bound electrons of C–H bonds render them inert in most circumstances. However, throughout the 1960s and 1970s, a large amount of crystallographic and spectroscopic evidence was amassed suggesting that TMs are capable of forming intramolecular interactions with the C–H bonds of appended ligands. By the early 1980s an irrefutable body of evidence existed showing that alkyl ligands can coordinate to a TM in an η^2 -fashion, with the primary M–C bond being augmented by a significant secondary interaction involving an unusually short C–H \cdots M contact. Green *et al.* reported the original and subsequent textbook examples of α - and β -C–H \cdots M interactions in TM alkyl complexes; *viz.* $[\text{RTiCl}_3(\text{dmpe})]$ (R = Me or Et).⁵

Agostic interactions are difficult to pin down by standard spectroscopic techniques, with NMR and IR spectroscopy often being unable to distinguish weak – and often fluxional – C–H \cdots M interactions from normal metal-alkyl C–H moieties. X-ray crystallography is also beset by significant problems in characterising the C–H \cdots M unit. For whilst an agostic structure can often be inferred by the corresponding distortion in the alkyl ligand, the H atom is often impossible to locate with any precision, causing particular difficulties in the case of α -C–H \cdots M interactions. Very few agostic complexes have been studied by neutron diffraction, but one notable success is $[\text{CH}_3\text{TiCl}_3(\text{dmpe})]$, Fig. 2(a), for which the geometry was

makes a close approach to the metal centre with a Ti–C–H angle of 93.5° and Ti \cdots H distance of 2.54 \AA .⁵

Brookhart and Green recognized the importance of such an interaction to fundamental organometallic transformations such as C–H activation and α - and β -hydride elimination, and coined the term ‘agostic’ to describe the phenomenon. The discovery of agostic interactions led to a major reassessment of the chemical behaviour of saturated organic ligands. Many large-scale catalytic processes, such as hydroformylation and Ziegler–Natta polymerisation, proceed by mechanisms which involve an agostic interaction in one or more of the critical steps. A ubiquitous reaction in organometallic chemistry is cyclometallation, a reversible process by which the a metal alkyl is converted into the corresponding metal alkene or arkyldiene hydride. All these reactions had been considered to proceed through a transition state involving C–H \cdots M interactions: the realisation that such a situation can actually represent the ground state in certain circumstances caused a revolution in the paradigm of organometallic chemistry. Numerous theoretical studies have confirmed the importance of agostic interactions in ground and transition states for these and related reactions.⁶

Two comprehensive reviews appeared in the 1980s, documenting the discovery and interpretation of agostic bonding in transition-metal systems.⁷ Brookhart and Green proposed the agostic interaction to involve a three-centre, two-electron (3c–2e) covalent bond, with donation of C–H bonding electrons into a vacant atomic orbital on the TM atom, although more recent theoretical studies favour a somewhat different description. In general, electron-deficient metals early in the transition series form agostic systems which are closer to the metal–alkyl representation, in which the degree of M \cdots H bonding is only modest. Electron-rich late TMs tend to form complexes which lie closer to an alkene–hydride situation, in which oxidative addition of the C–H bond to the TM centre is more advanced and is supported by the formally low oxidation-state metal centre.

The strength of agostic interactions is generally about 10 kJ mol^{-1} – similar to that of hydrogen bonds formed between organic molecules. Accordingly, these interactions are almost exclusively restricted to intramolecular situations: entropy effects will easily shake apart an intermolecular C–H \cdots M interaction. Only a handful of short-lived intermolecular agostic interactions have been detected using special spectroscopic techniques.⁸

In contrast, the Si–H moiety is both more polar and more polarizable than its C–H counterpart, permitting the stabilisation of intermolecular Si–H \cdots M bonding. Throughout the 1980s, a comprehensive series of studies by Schubert and others established the Si–H bond as a surprisingly good ligand.⁹ The general synthetic approach involves photochemical replacement of an M–CO bond with an $\text{M}(\eta^2\text{-SiH})$ moiety. Well over a hundred such silane complexes are now known, with those based on the metals in Groups 6–8 being particularly prevalent. Fig. 2(b) shows a representative example, $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\eta^2\text{-HSiFPh}_2)]$, the structure of which was determined by neutron diffraction.¹⁰ The Si–H distance, at 1.80 \AA , is about 20% longer than an uncoordinated Si–H bond, and the M–H distance of 1.57 \AA is close to that found in classical Mn hydrides.

The bonding in these complexes shares some similarities with agostic interactions, but lies closer to the oxidative addition product, as the frontier orbitals of the Si–H moiety, which constitute the donor and acceptor orbitals in the synergic interaction, are each more accessible than their C–H counterparts. As with agostic interactions, $\text{M}(\eta^2\text{-SiH})$ complexes play an important role in key organometallic transformations. A major industrial process is hydrosilation, whereby an Si–H moiety adds across the double bond of an alkene. The generally accepted cycle for this reaction invokes the so-called Chalk–Harrod mechanism, in which the H atom of a coordinated Si–H

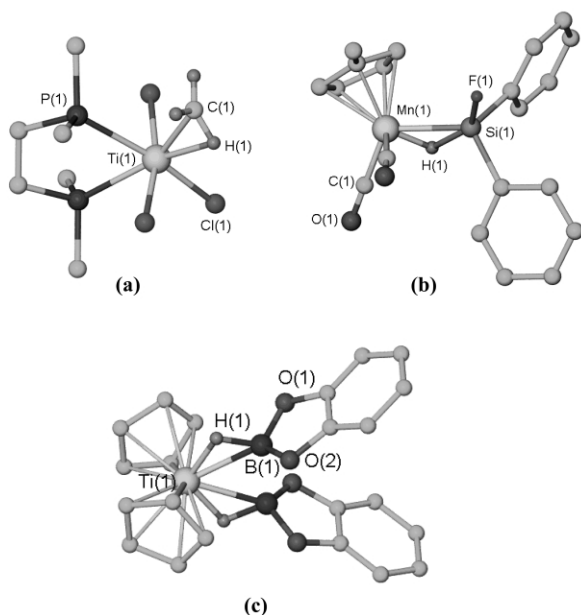


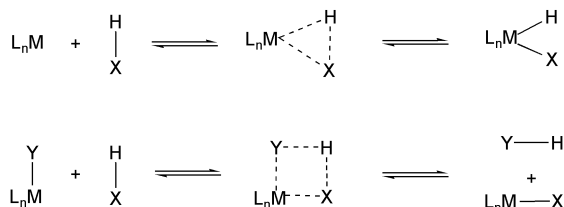
Fig. 2 Molecular structures of some representative TM σ -bond complexes: (a) $[(\text{dmpe})\text{TiCl}_3(\eta^2\text{-CH}_3)]$, (b) $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\eta^2\text{-HSiFPh}_2)]$, and (c) $[\text{Cp}_2\text{Ti}(\eta^2\text{-HBO}_2\text{C}_6\text{H}_4)_2]$. Redrawn from refs 5, 10 and 11b, respectively.

definitively pinned down by this technique. The methyl group was shown to be undistorted, but canted such that one C–H bond

bond migrates to the C atom of a neighbouring coordinated alkene, followed by reductive elimination of the saturated product. Hydrosilation reactions are central to the large-scale preparation of many types of silicone polymers.²

More recently, the B–H bonds of substituted boranes have been shown by Hartwig *et al.* to have a coordination chemistry similar to that of silanes, although to date only a few complexes have been isolated.¹¹ Fig 2(c) shows one example, [Cp₂Ti(η²-HBO₂C₆H₄)₂], which exhibits a double M···H–B interaction between Ti and catecholborane, with a Ti–H–B angle of 101° and a Ti···H distance of 1.74 Å. Hydroboration reactions have a vast utility in organic synthesis, and σ-borane complexes such as these are likely intermediates in many metal-catalysed hydroboration processes.²

Crabtree and Kubas have reviewed the phenomenon of σ-bond complexation by TM complexes.¹² Whilst there are significant differences between the bonding in agostic, silane and borane σ-complexes, they share a common feature: the η²-coordination of an E–H σ-bond to an unsaturated TM centre. This coordination permits them to take part in a wide range of characteristic organometallic reactions, such as insertion and migration. In addition, the ability of E–H bonds to coordinate at a TM centre opens up a new type of reactivity – σ-bond metathesis – whereby ligand exchange is mediated at the metal centre without formal oxidative addition taking place, as depicted in Scheme 2. Many early TM hydrides – including



Scheme 2 Comparison of reaction pathways for oxidative addition (above) and σ-bond metathesis (below) of a H–X moiety.

those with a d⁰ electron configuration which is unable to support oxidative addition – are able to effect H/D exchange with the C–H bonds of organic moieties by σ-bond metathesis. Activation of C–H bonds – in particular those of CH₄ – is a fundamentally important yet elusive process which has been achieved by only a handful of systems, most notably the photochemically generated moieties [CpIr(CO)] and [Cp*Ir(PMe₃)], which react with alkanes to give C–H oxidative addition products.¹³ Quantum chemical calculations and isotopic labelling experiments have shown methane activation barriers to be significantly lowered in this process by C–H bond coordination to the metal.⁶ The ability to understand and engineer σ-bond complexation permits chemists to encourage and exploit such challenging but valuable chemical transformations. In this respect, the recent isolation of [(PPri₃)₂RuH₂(η³:η³-μ-SiH₄)H₂Ru(PPri₃)₂] is particularly noteworthy: in this complex SiH₄ is coordinated between two TM centres, with significantly long Si–H bonds and very short Ru···Si distances.¹⁴

2.2 Molecular dihydrogen complexes

Oxidative addition of molecular hydrogen to TM complexes (Scheme 2) is an important and long-established synthetic route to TM hydrides, many of which have key roles in synthesis and catalysis. One of the major chemical advances of the 1980s was made in 1984, when Kubas reported the complex [(PPri₃)₂(CO)₃W(η²-H₂)], Fig. 3(a), the first example of a system containing intact molecular dihydrogen as a ligand.¹⁵ Many more such compounds were reported soon after: currently several hundred are known. These systems constitute a special class of σ-bond complex (*q.v.*). Excellent accounts have been

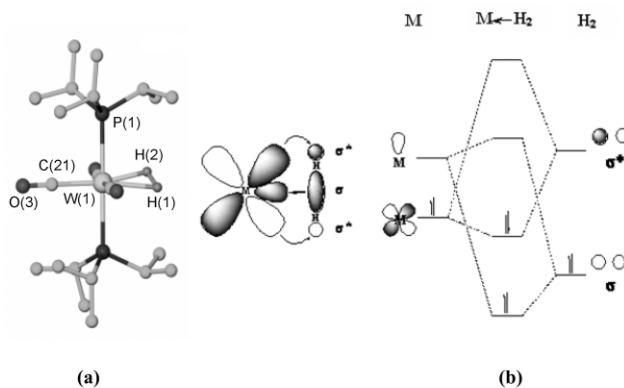


Fig. 3 (a) Molecular structure of the dihydrogen complex [(PPri₃)₂(CO)₃W(η²-H₂)], redrawn from ref. 15. (b) MO scheme showing the interaction between the frontier orbitals of H₂ and an ML₅ fragment. Adapted from ref. 16c.

published documenting the initial discovery and subsequent structural and chemical studies of dihydrogen complexes.¹⁶

Understanding how a TM centre can activate and cleave a strong, non-polar single bond like H–H is fundamental to exploiting the catalytic behaviour of TM complexes in the activation of small molecules. The bonding in M(η²-H₂) systems may be rationalised by a modified form of the Dewar–Chatt–Duncanson model which has proved so successful for TM–alkene complexes, as represented in Fig. 3(b).¹⁶ There is a synergic combination of ligand-to-metal donation from the H₂ HOMO and metal-to-ligand back-donation into the H₂ LUMO. As the HOMO is bonding and the LUMO antibonding with respect to the H–H moiety, each component of the interaction serves to weaken the H–H bond. Accordingly, in complexes such as [(PPri₃)₂(CO)₃W(η²-H₂)], where there is a prevalence of strong π-acceptor ligands, the degree of back-donation to H₂ is modest and the dihydrogen moiety remains intact. In contrast, systems like [(PPh₃)₃RhCl] (Wilkinson's Catalyst), which have a much more electron-rich metal centre, promote full oxidative addition of H₂ to give a dihydride complex.² Almost all dihydrogen complexes have the metal in a low-spin d⁶ configuration: in a *pseudo*-octahedral environment this corresponds to full occupation of the T_{2g} orbitals, providing an optimal environment to furnish the metal–H₂ back-bonding which supports the dihydrogen ligand.

As well as ligand effects, the nature of the metal has a significant bearing on the balance between dihydrogen and dihydride forms. Classical hydrides are preferred for metals with more diffuse d orbitals, and there is a general trend from classical to non-classical behaviour as the transition series is crossed. Likewise, within a triad the classical hydride form is favoured for the heavier metals. For example, the Group 8 metals form a series of complexes of the form [(PR₃)₃MH₄], in which the Fe and Ru systems are mixed MH₂(η²-H₂) entities, whereas Os forms a genuine tetrahydride.¹⁷ Dihydrogen complexes are generally scarce for third-row TMs, as the favourable M(5d)–H(1s) orbital overlap drives oxidative addition to completion.

Neutron-diffraction studies have provided accurate structural characterisation of the M(η²-H₂) moiety in several instances. For example, the Kubas complex displays W–H distances of 1.89 Å, about 10% longer than classical W–H moieties. The H–H distance of 0.82 Å is also elongated by 10% compared to free H₂.¹⁶ This contrasts with a *cis* H···H separation of 2.30 Å in an octahedral complex like *fac*-[(PPh₂Me)₃IrH₃].³ However, discrimination between the classical and dihydrogen forms of many TM hydride complexes on the basis of spectroscopic techniques is often not straightforward. The ¹H NMR chemical shifts of M(η²-H₂) and MH₂ each occur in the hydride region of the spectrum (*ca.* 0 – –30 ppm). However, two elegant NMR methods have proved invaluable in the characterisation of dihydrogen complexes.¹⁶ The first involves the incorporation of

HD in place of H₂ into the complex and subsequent measurement of the H–D coupling constant, which has a value of 43.2 Hz in free HD. In dihydrogen complexes, where a significant degree of direct H⋯H bonding is retained, ¹J_{HD} values greater than 25 Hz are generally observed. Dihydride complexes, with no residual H–H bonding, exhibit ²J_{HD} values less than 5 Hz. The second NMR method relies on the efficient relaxation mechanism provided for a ¹H nucleus by a second proton in close proximity: the T₁ (spin-lattice) relaxation mechanism is dominated by this dipole–dipole contribution, which displays an (r_{HH})^{−6} distance dependence. Hence, T₁ values for ¹H nuclei in dihydrogen complexes are significantly shorter (< 160 ms) than their dihydride counterparts (> 300 ms) at 500 MHz. In practice, T₁ is temperature-dependent, and the maximum relaxation rate, corresponding to T₁(min), is usually recorded. This method sometimes gives less than clear-cut conclusions in the case of polyhydride complexes (*q.v.*).

Both J_{HD} values and T₁ measurements afford reliable estimates of the H⋯H distance in solution. Surprisingly, they revealed a class of complexes whose ¹J_{HD} and T₁(min) values fall between the extremes expected for dihydrogen and dihydride systems, with corresponding H⋯H distances ranging from 0.8 Å to greater than 1.1 Å. Accurate measurements from neutron-diffraction and solid-state NMR spectroscopy also revealed a number of remarkably large H⋯H separations. It was eventually realised that there exists a continuous spectrum of H⋯H distances in TM hydride complexes, ranging from 0.8 Å (dihydrogen) through 1.1 Å (stretched dihydrogen) and 1.3 Å (compressed dihydride) to greater than 1.6 Å (dihydride). A range of Os complexes studied by Morris, shown in Fig. 4,

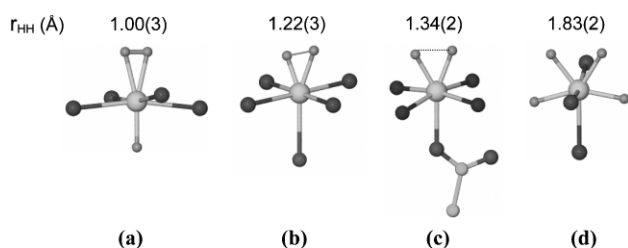


Fig. 4 Metal coordination environment in a series of osmium hydride complexes showing progressive stages on the reaction coordinate to oxidative addition of H₂. Redrawn from ref. 18. (a) [(dppe)₂OsH(H₂)]⁺, (b) [(dppe)₂OsCl(H₂)]⁺, (c) [(en)₂OsH(H₂)]⁺, and (d) [(PMe₂Ph)₃OsH₄]. The H⋯H distances are characteristic of complexes containing dihydrogen, stretched dihydrogen, compressed dihydride and classical dihydride ligands, respectively.

elegantly shows the continuum of H⋯H distances which occur in the transition from dihydrogen to dihydride behaviour as the associated ligand set at the metal is altered.¹⁸

Vibrational spectroscopy has also proved to be a valuable technique in characterising dihydrogen complexes.¹⁶ Classical TM hydrides display M–H stretching vibrations in the region 1700–2300 cm^{−1}, and deformation modes around 700–900 cm^{−1}. A [L_nM(η²-H₂)] complex gives rise to six modes of vibration associated with the triatomic MH₂ moiety, but only rarely have all six been identified for a particular complex. Most striking is a feature corresponding mainly to an H–H stretching motion, which occurs at 2400–3200 cm^{−1}, whilst modes primarily associated with antisymmetric and symmetric MH₂ stretching occur around 1300–1600 and 850–1000 cm^{−1}, respectively. These frequencies are lower than their counterparts in classical M–H complexes, on account of a smaller metal–hydrogen force constant and a greater reduced mass; the deformation modes of the M(η²-H₂) fragment are likewise lowered in frequency. Stretching and bending motions are not strictly separable in a simple cyclic triatomic unit, and accordingly the above descriptions are only approximate. Indeed, the significant IR intensity of the ‘H–H stretching’ vibration is a consequence of the hybrid nature of the motion.

The response of the stretching modes to partial isotopic substitution is diagnostic of the M(η²-H₂) moiety: whilst an H–M–D dihydride exhibits distinct M–H and M–D stretching vibrations, M(η²-HD) displays modes at frequencies approximately halfway between those of its H₂ and D₂ counterparts.

The torsional mode arising from rotation of the H–H ligand about the L_nM–H₂ vector occurs around 350 cm^{−1}, and has proved to be a rich source of information about the M–H₂ bonding interaction.¹⁹ As the σ-component of this interaction has no directional character, it is the π-contribution – *i.e.* the M–H₂ back-bonding, which determines the rotational potential. As this component also controls H–H bond fission, the potential increases with increasing H⋯H distance. In the limit a dihydride results and H₂ rotation ceases. The orientation of the H₂ ligand can reveal more subtle features of the M–H₂ bonding interaction. For example, in [Cp*Ru(dppm)(η²-H₂)]⁺ the H–H vector lies parallel to the Cp* ligand, where it can optimise overlap of its σ* orbital in the piano-stool complex with the occupied dπ-bonding orbital on the Ru centre.

The transition from dihydrogen to classical hydride is less clear-cut and subtler than was initially thought. The spectrum of H⋯H distances found in the Os complexes shown in Fig. 4 reveals oxidative addition of H₂ to be a process with a surprisingly long path on the reaction coordinate, and one which is influenced strongly by the nature of the metal and its associated ligands. The kinetics and thermodynamics of H₂ binding also imply a surprisingly wide spectrum of behaviour.¹⁶ Many complexes, such as [(PPh₂Et)₃FeH₂(η²-H₂)]⁺, are labile in solution and can be manipulated only at low temperatures under an atmosphere of H₂. In contrast, some cationic dihydrogen complexes are remarkably inert; for example, [CpRu(dmpe)(η²-H₂)]⁺ is indefinitely stable in refluxing THF. Quantitative studies have provided estimates of the strength of H₂ binding to the metal centre in several instances. For example, the interaction energy between H₂ and the naked fragments [W(CO)₃(PCy₃)₂] and [Cr(CO)₅] has been estimated at −105 and −70 kJ mol^{−1}, respectively; in good agreement with M–H₂ bond dissociation energies predicted by quantum chemical calculations.¹⁶

In several instances, a dihydrogen complex has actually been found to exist in equilibrium with the corresponding dihydride.¹⁶ The original system of Kubas is the classic example, with [(PPR₃)₂(CO)₃(H₂)] displaying a 4:1 mixture of M(η²-H₂) and MH₂ versions at room temperature, and ΔG[‡] for oxidative addition being *ca.* 60 kJ mol^{−1}. The cation [Cp*Ru(dmpe)(η²-H₂)]⁺ also exists in a 6:1 equilibrium mixture with its classical tautomer: here ΔG[‡] was measured at 85 kJ mol^{−1}. Such high barriers to formation of MH₂ indicate a deep well for the M(η²-H₂) precursor, making it kinetically rather stable. Not only are they consistent with the large number of dihydrogen complexes now known, they are also in keeping with the long path length on the reaction coordinate to full oxidative addition evident in Fig. 4, which results from the increase in metal coordination number attending H–H bond rupture: as the H₂ ligand occupies a single coordination site, an H–M–H arrangement necessarily requires an extra site, with concomitant rearrangement of the whole ligand set at the metal.¹⁶

In addition to homolytic cleavage of the H–H bond to give an H–M–H dihydride, coordinated H₂ is also significantly activated with respect to heterolytic cleavage. Free H₂ is a very weak acid (pK_a = 35), but the weakened H–H bond in the dihydrogen ligand is dramatically activated with respect to heterolysis by coordination at a metal centre. For example, [(dppe)₂FeH(η²-H₂)]⁺ has a pK_a of 13. Strongly Lewis-acidic centres show an even more striking effect: the pK_a of [(dppe)₂Ru(CO)(η²-H₂)]⁺ has been estimated to be as low as −6.²⁰ Deprotonation appears also to be kinetically more favourable for dihydrogen than for hydride ligands. Thus, [(PPh₃)₂Ir(bq)(η²-H₂)]⁺ loses H⁺ from the coordinated H₂ ligand rather than the Ir–H moiety, and [CpRu(dmpe)(η²-H₂)]⁺

is deprotonated more rapidly than its classical tautomer $[\text{CpRu}(\text{dmpe})\text{H}_2]^+$.¹⁶ The principle of microscopic reversibility implies that the reverse reaction – protonation of the neutral hydride – will initially result in a dihydrogen complex. Such a situation is well established: protonation of an M–H bond almost always occurs in preference to direct protonation at the metal centre, even when the resulting dihydrogen complex has no independent existence. For example, the dihydrogen species $[\text{Cp}^*(\text{PCy})_3\text{RuH}(\eta^2\text{-H}_2)]^+$ was demonstrated to be a low-temperature intermediate in the protonation of $[\text{Cp}^*(\text{PCy})_3\text{RuH}(\eta^2\text{-H}_2)]$.²¹ As with oxidative addition of H_2 , there is a change in coordination number required for protonation or deprotonation at a metal centre. This is not necessitated for the alternative pathway involving an M–H bond, which thus represents a much more favourable route for transfer of H^+ to or from a TM complex.

Quantum chemical calculations have been used to good effect to explore the structure, bonding and reactivity of many dihydrogen complexes, and in some cases have provided unique insights into these aspects of their chemistry. For example, the series $[(\text{PH}_3)_3\text{MH}_4]$ ($\text{M} = \text{Fe}, \text{Ru}$ or Os), was shown by DFT methods to model the behaviour observed experimentally for $[(\text{PR}_3)_3\text{MH}_4]$ systems (*q.v.*). However, non-relativistic calculations implied that all three metals favour a $[(\text{PH}_3)_3\text{MH}_2(\eta^2\text{-H}_2)]$ ground state, and only when relativistic functionals were included for Os did the resulting destabilisation of the 5d orbitals tip the balance in favour of $[(\text{PH}_3)_3\text{OsH}_4]$.²²

Since the discovery of dihydrogen complexes in the 1980s, many polyhydride complexes have been suspected of harbouring non-classical $\text{M}(\eta^2\text{-H}_2)$ moieties. Whilst no polyhydride system has been shown by diffraction to contain a *bona fide* dihydrogen ligand, $[(\text{PMe}_2\text{Ph})_3\text{Re}(\text{CO})\text{H}_4]^+$ exhibits J_{HD} and T_1 values in solution indicative of such a situation, and on similar grounds the complexes $[\{(p\text{-C}_6\text{H}_4\text{Me})_3\text{P}\}_2\text{ReH}_7]$ and $[(\text{PMe}_2\text{Ph})_3\text{OsH}_5]^+$ each exhibit short $\text{H}\cdots\text{H}$ contacts which fall in the regime of stretched dihydrogen complexes.¹⁶ The stereochemical non-rigidity of polyhydrides with coordination numbers greater than six is well established, and can occur by low-energy framework deformations such as pseudorotation and turnstile processes, which require neither a change in the metal oxidation state nor extensive ligand rearrangement. Crabtree *et al.* explored the possibility that this fluxionality is mediated by low-lying dihydrogen moieties, but found no conclusive evidence in favour of such a suggestion.²³

2.3 Comparison between different types of σ -bond complexes

The general interaction between a TM centre and an X–H moiety (where $\text{X} = \text{C}, \text{Si}, \text{B}$ or H) can be usefully discussed with reference to the MO scheme presented for dihydrogen complexes (Fig. 3). The degrees of X–H-to-metal donation and metal-to-X–H back-donation depend on the energies of the HOMO and LUMO of the X–H moiety; respectively: these frontier orbitals correspond to the X–H bonding and antibonding orbitals. Thus, whilst a whole spectrum of behaviour can be identified within each class of σ -bond complex, some generalisations can be made. Strong and non-polarisable C–H bonds, with a low-lying HOMO and a prohibitively high LUMO, engage in only a modest interaction with a metal centre, and are often structurally and spectroscopically similar to their unperturbed counterparts. The more polarisable H–H moiety is characterised by a higher HOMO and a more accessible LUMO, and hence interacts more strongly with the metal. Even more polarisable and basic is the Si–H moiety, which engages in a stronger interaction: indeed, many silane complexes are best considered as late stages on the reaction coordinate to oxidative addition, or even as silyl hydrides which exhibit secondary interactions between the Si and H ligands (*q.v.*). Borane

complexes present some significant differences from other TM σ -bond complexes: the availability of a vacant p-orbital at boron permits more efficient back-donation of electron density from the metal than is the case for Si–H moieties. However, oxidative addition of the B–H unit is arrested, as the Lewis-acidic boron centre accepts electron density from the metal which would be otherwise destined for the B–H σ^* -orbital.

3 Hydrogen-bonding effects in TM hydride complexes

In classical hydrogen bonds of the form $\text{A}-\text{H}\cdots\text{B}$, a weak acid A–H is the donor, and the acceptor B is usually an electronegative atom like N, O or F carrying a lone pair. This description was subsequently extended to include π -electron density as an H-bond acceptor. Since about 1990, however, two new classes of hydrogen bond have emerged in which the acceptor B is a TM complex. In the first case, an electron pair in a non-bonding metal orbital acts as the acceptor. In the second case, the acceptor is the σ -bonding pair of the M–H bond, which produces a relatively electron-rich H atom.

3.1 $\text{M}\cdots\text{H}-\text{X}$ Hydrogen bonding

In 1991, Brammer *et al.* observed $\text{N}-\text{H}\cdots\text{Pt}$ interactions in the unusual diplatinum salt $[\text{Pr}^n_4\text{N}]_2[\text{PtCl}_4]\text{cis}[\text{PtCl}_2(\text{NH}_2\text{Me})_2]$, Fig. 5(a), with the vacant axial site of the square-planar

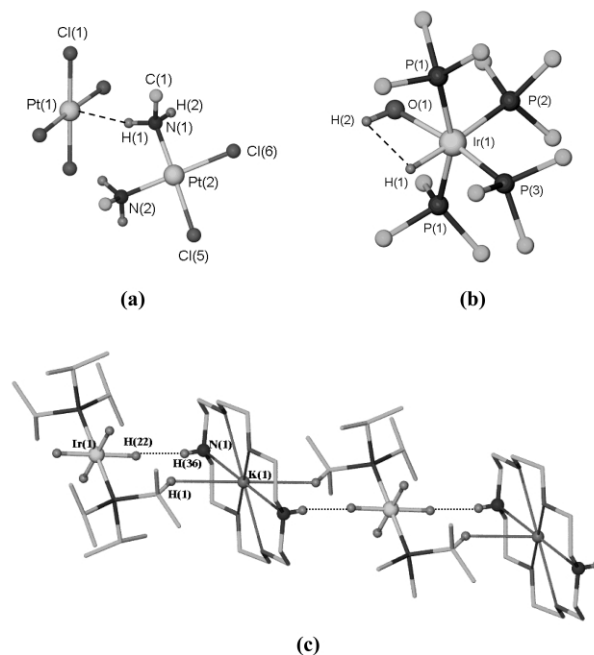


Fig. 5 Solid-state structures of (a) $[\text{Pr}^n_4\text{N}]_2[\text{PtCl}_4]\text{cis}[\text{PtCl}_2(\text{NH}_2\text{Me})_2]$, (b) $[(\text{PMe}_3)_4\text{IrH}(\text{OH})]^+$, and (c) $[\text{K}(\text{1,10-diaza-18-crown-6})][(\text{PPt}_3)_2\text{IrH}_4]$. Redrawn from refs 24, 28 and 33, respectively. Systems (a) and (b) display $\text{M}\cdots\text{H}-\text{X}$ and $\text{M}-\text{H}\cdots\text{H}-\text{X}$ hydrogen bonding, respectively; whilst (c) exemplifies how $\text{M}-\text{H}\cdots\text{H}-\text{X}$ interactions can be used to control supramolecular architecture.

$[\text{PtCl}_4]^{2-}$ ion showing a close approach of an amine N–H bond.²⁴ The $\text{Pt}\cdots\text{H}$ distance of 2.26 Å and the near-linear N–H–Pt angle of 167° in the neutron diffraction structure indicated an interaction between the occupied Pt d_{z^2} orbital and the amine N–H bond.

A similar phenomenon was shown by neutron diffraction to occur in the structurally simpler ion pairs $[\text{R}_3\text{NH}]^+[\text{Co}(\text{CO})_4]^-$, with elongated N–H bonds and a short $\text{H}\cdots\text{Co}$ distance of 2.50 Å, the anion distorting from regular tetrahedral symmetry towards a distorted trigonal bipyramid. Increasing the basicity

of the Co centre by replacing CO with phosphine ligands resulted in a stronger interaction.²⁵ The spectroscopic properties of these systems were found to reflect the structural changes wrought by the interaction, with the N–H proton displaying a shift to high frequency in the NMR spectrum and the IR spectrum revealing a reduction in the N–H stretching frequency. More sophisticated spectroscopic studies revealed a reduction in the ^1H – ^{15}N NMR coupling constant in analogous N–H \cdots Pt systems,²⁶ and an IR study of the interaction between acidic alcohols and a series of 18-electron complexes of Co, Rh and Ir showed a lowered O–H stretching frequency characteristic of O–H \cdots M hydrogen bonding.²⁷

3.2 M–H \cdots H–X Hydrogen bonding

In 1990, Milstein *et al.* reported a neutron-diffraction structure of a salt of the $[(\text{PMe}_3)_4\text{Ir}(\text{OH})]^+$ cation, Fig. 5(b), which revealed a close approach of 2.4 Å between the hydroxyl proton and the hydride ligand, at the limit of the van der Waals contact distance.²⁸ In 1994, the groups of Crabtree and Morris simultaneously prepared cationic Ir hydride complexes with even shorter M–H \cdots H–X contacts.²⁹ Crabtree reported the structure of $[(\text{C}_6\text{H}_5\text{N})\text{N}=\text{C}(\text{OH})\text{Me}\}\text{IrH}_2(\text{PPh}_3)_2]^+$, which showed the amide group in the ligand to be present as its rare iminol tautomer on account of an H \cdots H interaction between the Ir–H bond and H–O bonds. NMR T_1 measurements in solution (*q.v.*) gave an H \cdots H distance of only 1.8 Å, and the ^1H NMR spectrum showed a 3 Hz coupling between the Ir–H and O–H protons, the strength of the interaction being estimated at 18 kJ mol $^{-1}$. Morris *et al.* prepared a salt of the complex $[(\text{C}_5\text{H}_5\text{NS})_2\text{IrH}_2(\text{PCy}_3)_2]^+$, whose X-ray diffraction structure showed two close Ir–H \cdots H–N contacts, estimated at 1.75 Å by T_1 measurements. Intermolecular Re–H \cdots H–N bonds were subsequently shown by Crabtree *et al.* to be present in the complex formed between $[(\text{PPh}_3)_3\text{ReH}_5]$ and indole.³⁰

IR studies of a series of intermolecular M–H \cdots H–X systems demonstrated that the strength of the interaction correlates with the acidity of X–H and with the basicity of M–H, and gave bond energies falling in the range 10–40 kJ mol $^{-1}$.³¹ Hence the interaction is comparable to a conventional hydrogen bond of medium strength, a remarkable situation for a weak acid/weak base interaction. However, the H–H covalent bond is the strongest homonuclear single bond known, and the polarisable M–H moiety may well permit a significant covalent contribution to augment what is a formally electrostatic interaction. Hundreds of systems displaying M–H \cdots H–X bonding are now known. The interaction is generally termed a proton-hydride or dihydrogen bond, although the latter terminology should not be confused with the bonding in molecular dihydrogen complexes (Section 2.2). The phenomenon has been the subject of several recent reviews.³²

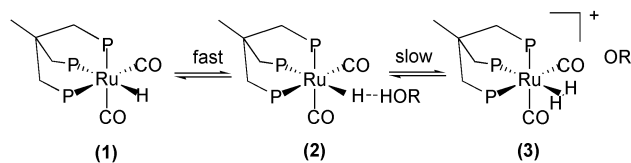
The M–H \cdots H moiety in M–H \cdots H–X systems is invariably bent, in contrast to classical A–H \cdots B and M \cdots H–X systems, which approach linearity. The possibility that the binding arises in fact from an M \cdots H–X interaction with lone pairs on the metal centre was discounted when it was shown that d^0 systems like $[(\text{dppe})\text{ReH}_7]$ participate as enthusiastically as do d^2 systems like $[(\text{PPh}_3)_3\text{ReH}_5]$.^{32c} Morris and his group have exploited the supramolecular potential of the interaction to construct an elegant series of polymers based on alkali metal cations and polyhydride anions. For example, the system $[\text{K}(1,10\text{-diaz-18-crown-6})][(\text{PPr}'_3)_2\text{IrH}_4]$, Fig. 5(c), forms a structure based on infinite one-dimensional chains held together with proton-hydride bonds.³³

3.3 General considerations regarding hydrogen bonding

A hydrogen bond A \cdots H \cdots B is effectively an arrested proton transfer from A to B, with the ultimate position of the proton

along the reaction coordinate being determined by the relative basicities of A and B. Accordingly, the M \cdots H–X interactions seen in systems like $[\text{R}_3\text{NH}]^+[\text{Co}(\text{CO})_4]^-$ may also be viewed as representing the vestigial Co–H bond in the alternative representation M–H \cdots X. The vast majority of M–H moieties are characterised by a hydrogen moiety which carries a substantial partial negative charge. However, the neutral complex $[\text{HCo}(\text{CO})_4]$ is a member of the class of acidic carbonyl hydrides, and with a $\text{p}K_a$ of 1 is comparable with a strong mineral acid like H_2SO_4 .² A basic amine will clearly abstract such an acidic proton.

In Section 2.2, the preparation of dihydrogen complexes by protonation of an M–H moiety with a strong acid was described. Use of weaker acids leads instead to the type of incomplete proton transfer seen in proton-hydride hydrogen bonding. Indeed, H-atom exchange between the M–H and H–X components of the interaction has been shown to occur readily in $[(\text{C}_6\text{H}_5\text{N})\text{N}=\text{C}(\text{OH})\text{Me}\}\text{IrH}_2(\text{PPh}_3)_2]^+$, being mediated by a putative dihydrogen intermediate in which the H–H moiety rotates in place (*q.v.*) before reverting to the proton-hydride formulation.^{32c} The M–H \cdots H–X distances characterised for proton-hydride interactions, falling in the range 1.3–1.8 Å, are comparable with the H \cdots H distances in stretched dihydrogen complexes (Section 2.2), implying that the two types of system have much in common. An elegant NMR study by Shubina and Epstein has characterised the reaction coordinate for protonation of $[(\text{triphos})\text{Ru}(\text{CO})\text{H}_2]$ by $(\text{CF}_3)_2\text{CHOH}$ to give $[(\text{triphos})\text{Ru}(\text{CO})\text{H}(\eta^2\text{-H}_2)]^+$.^{32d} This has revealed a significant activation barrier of around 50 kJ mol $^{-1}$ separating the Ru–H \cdots H–O intermediate from the cationic product, as depicted in Scheme 3.



Scheme 3 Reaction stages for the protonation of $[(\text{triphos})\text{Ru}(\text{CO})\text{H}_2]$ (1) to give $[(\text{triphos})\text{Ru}(\text{CO})\text{H}(\eta^2\text{-H}_2)]^+$ (3) via the hydrogen-bonded intermediate $[(\text{triphos})\text{Ru}(\text{CO})\text{H}_2]\cdots\text{HOCH}(\text{CF}_3)_2$ (2). R = $(\text{CF}_3)_2\text{CH}$.

Proton-hydride bonding is now a well-established phenomenon in the structures determined for many TM hydride complexes. However, its existence as a pervasive but silent interaction in solution may be even more important. The kinetic preference for TM hydride complexes to protonate at the M–H bond, rather than at the metal centre (Section 2.2), is consistent with a M–H \cdots H–X precursor providing a low-energy approach trajectory, quite apart from any metal-based kinetic factors relating to changes in coordination environment. The reactivity of TM hydrides may be altered by proton-hydride interactions in solution. For example, Chu *et al.* have shown the catalytic hydrogenation of CO_2 to formic acid by the complex $[(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{NMe}_2\text{H})\text{RuH}(\text{dppm})]^+$ to be assisted by an intramolecular Ru–H \cdots H–N interaction in the rate-determining step.^{34a} and Noyori's group has demonstrated that the reaction of $[(\eta^6\text{-C}_6\text{R}_6)\text{RuCl}_2]$ with chiral diamines produces complexes with proton-hydride bonds, which catalyse efficiently the asymmetric hydrogenation of ketones to chiral alcohols.^{34b,c} Low-lying dihydrogen intermediates accessed by formation of M–H \cdots H–X interactions can also play an important role in facilitating the type of reaction known as σ -bond metathesis, depicted in Scheme 2.

4 Quantum mechanical effects in TM hydride complexes

The hydrogen nucleus with its single proton is uniquely susceptible to quantum mechanical effects on account of its low

mass. The most common manifestation of these effects is tunnelling, whereby the wavefunction of a light particle can penetrate through a classical potential without having sufficient energy to surmount the barrier. The distance through the barrier determines the rate of attenuation of the wavefunction, so the classical barrier height indirectly affects the quantum mechanical behaviour.

However, if two similar H-atom potentials lie sufficiently close together (*i.e.* are connected by a short path length on the reaction coordinate), then the proton wavefunction can emerge in an adjacent potential and interfere with the indigenous wavefunction in this neighbouring well. The symmetric and antisymmetric combinations resulting from this interference give rise to two states slightly different in energy, and the transition between them can be measured by an appropriate technique. This situation is depicted in Fig. 6(a). H-atom

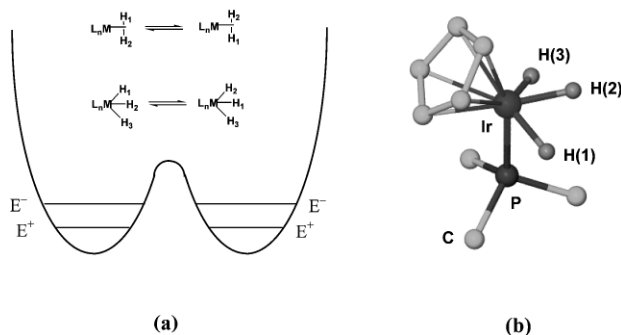


Fig. 6 (a) Double-well potential with a low barrier, showing splitting of the vibrational levels caused by quantum mechanical tunnelling. The symmetric and antisymmetric states are represented as E^+ and E^- , respectively. The permutation of H-atom positions giving rise to tunnelling effects in the spectra of TM dihydrogen and trihydride complexes is also depicted. Adapted from ref. 38. (b). Molecular structure of $[\text{CpIr}(\text{PMe}_3)\text{H}_3]^+$, as determined by neutron diffraction, showing the planar MH_3 moiety. Redrawn from ref. 37.

tunnelling is a well-established phenomenon in many chemical systems, the textbook example being the umbrella inversion of ammonia, which exhibits an absorption in the microwave region of the spectrum corresponding to a splitting of 36 cm^{-1} .

4.1 Tunnelling effects in dihydrogen complexes

Tunnelling phenomena in dihydrogen complexes were first observed in the 1980s, when it was recognised that H_2 rotation about the metal– H_2 bond (Section 2.2) is characterised by a double-well potential with a low classical barrier ($1\text{--}10\text{ kJ mol}^{-1}$) and a short reaction path ($\pi/2$ times the H–H distance). This gives rise to two states with an energy difference of the order of $1\text{--}20\text{ cm}^{-1}$, which falls in the microwave region of the electromagnetic spectrum (around 10^{11} Hz). Inelastic neutron scattering (INS) is an ideal technique for studying the phenomenon, as the neutron has effectively the same mass as the proton – making for efficient momentum transfer – and the large incoherent scattering cross section of the ^1H nucleus results in high intensity. Furthermore, the symmetric-to-antisymmetric nature of the transition corresponds to a spin flip in the H_2 moiety: spin is thus conserved as the neutron is scattered. In studying several dozen dihydrogen systems by INS, Albinati and Eckert have shown the H_2 rotational tunnelling rate to correlate inversely with the classical barrier height which results from the degree of back bonding provided by the metal centre.¹⁹ The hydrogen-neutron interaction gives rise to inelastic features which appear as wings on either side of the elastically scattered monochromatic neutron beam, in a manner which has many similarities with Raman spectroscopy.

Transitions in systems with barriers higher than about 12 kJ mol^{-1} are not observable by INS.

4.2 Tunnelling effects in trihydride complexes

In the early 1980s the complex $[\text{Cp}_2\text{NbH}_3]$ was reported to show anomalously broad peaks in the hydride region of the ^1H NMR spectrum, which displayed a puzzling temperature dependence.³⁵ This remained an oddity until the end of the decade, when Chaudret and co-workers prepared a series of substituted cyclopentadienyl versions of this complex and found a substituent-dependence of J_{HH} opposite to that expected. These workers also prepared a series of complexes of the form $[\text{Cp}^*\text{Ru}(\text{PR}_3)\text{H}_3]$ whose J_{HH} values were also temperature-dependent and reached almost 200 Hz .³⁶ About the same time, similar behaviour was reported by Heinekey *et al.* for analogous $[\text{CpIr}(\text{PR}_3)\text{H}_3]^+$ systems, resulting in the proposal that the unprecedented trihydrogen ligand was responsible for the peculiar NMR properties observed for these complexes. Such a situation was refuted by the structure of a salt of $[\text{CpIr}(\text{PMe}_3)\text{H}_3]^+$, determined by neutron diffraction; the shortest H...H distance between the hydride ligands at 1.67 \AA , ruled out a significant bonding interaction between them.³⁷

At this stage it was realised that a quantum mechanical effect must be responsible for the remarkable NMR properties of these trihydride systems. Definitive proof came from the quenching of the effect caused by substitution of one or more of the hydrides by deuterium. The two equivalent hydride representations $\text{H}_1\text{H}_2\text{H}_3$ and $\text{H}_2\text{H}_1\text{H}_3$, can be represented by a double-well potential, as shown in Fig. 6(a), and can interconvert by tunnelling. This gives rise to an exchange coupling (J_{ex}), which augments the classical Fermi contact coupling between the ^1H nuclei (J_{mag}), according to the equation $J_{\text{HH}} = J_{\text{mag}} - 2J_{\text{ex}}$. The sign of J_{mag} may be positive or negative, whilst that of J_{ex} is inherently negative. As the temperature increases, population of higher pairs of vibrational levels within the two wells leads to an increase in vibrational amplitudes and more efficient tunnelling, causing a sharp increase in J_{ex} . Hence many trihydride systems display J_{HH} values which decrease, pass through zero, then increase as the temperature is raised.³⁸

Exchange couplings are generally large, ranging from $50\text{--}1000\text{ Hz}$, but systems with values as high as $45\,000\text{ Hz}$ have been reported, exceeding by orders of magnitude the J_{HH} value of 280 Hz measured for dihydrogen. The temperature- and ligand-dependence of J_{HH} are found to accord with the double-well model, showing at low temperatures a first-order AB_2 pattern, which progresses through second order behaviour to give coalescence as the ratio $J/\Delta\nu$ changes. The tunnelling splitting for such non-bonded hydride exchange is much smaller than that for dihydrogen exchange (Section 4.1), explaining why it is observed by a radio-frequency technique like NMR. Exchange coupling of electrons in the ESR spectra of biradicals is a well-known phenomenon, but the observation of a similar effect for the much more massive proton is rare. Trihydrides which tunnel at a rate of approximately $1\text{--}10^5\text{ Hz}$ show these exchange couplings, corresponding to ΔG^\ddagger values in the range $35\text{--}70\text{ kJ mol}^{-1}$. Systems which tunnel more slowly than this will not display J_{ex} in their NMR spectra, whilst those which tunnel faster may appear to be classically fluxional. Furthermore, the existence of a low classical barrier and short tunnelling path length are necessary, but not sufficient, conditions for the observation of quantum mechanical exchange. For example, the complex $[(\text{PPh}_3)_2(\text{SiPh}_3)\text{ReH}_6]$ has a classical exchange barrier of 44 kJ mol^{-1} , but does not exhibit quantum mechanical coupling, possibly because global ligand rearrangement in the fluxional complex impedes the tunnelling process.³⁹

Whilst the origin of these trihydride couplings is unquestionably quantum mechanical, the dynamics of the process by which

the proton wavefunctions overlap remains open to some debate. Initial models considered a linear (in-plane) H–H bending motion to bring H₁ and H₂ sufficiently close to each other. Later suggestions proposed this H₁/H₂ exchange to occur by a rotational (out-of-plane) mechanism, mediated through an equilibrium with a low-lying M(H)(η^2 -H₂) dihydrogen-hydride. It is now generally believed that a combination of both in-plane and out-of-plane MH₂ bending contributes to a ‘lift-off’ motion, which appears then to proceed by rotational tunnelling, with a short H...H distance rather than the presence of H–H bonding being the critical factor.^{36,38}

The tunnelling frequency, and hence J_{ex} , is very sensitive to small changes in the chemical and physical environment of the MH₃ moiety. For example, adding electron-withdrawing SiMe₃ groups to the cyclopentadienyl ligands in [Cp₂NbH₃] causes J to increase from 4 to 70 Hz, and Lewis acids such as AlH₃ bind to one of the outer M–H bonds in [Cp₂NbH₃], also to cause an increase in the value of J_{ex} . Each of these chemical perturbations stabilises the dihydrogen-hydride form believed to mediate the exchange.^{40a} In an elegant experiment, Ernst *et al.* demonstrated that a pressure of 5 kbar leads to a reduction in solvent volume, which hinders the vibrational motions of the MH₃ moiety and hence reduces J_{ex} .^{40b}

Quantum mechanical exchange effects in the ¹H NMR spectrum have been found for dozens of TM trihydrides, although not all [L_nMH₃] systems display them. For example, the structure of [(dppe)₂Fe(H)(η^2 -H₂)]⁺ enforces a *trans* disposition of hydride and dihydrogen ligands which precludes exchange, and [Cp*Rh(PMe₃)H₃]⁺ has been found to have a clearly defined dihydrogen-hydride ground state, in contrast to its Ir analogue which shows exchange coupling.⁴¹ Sandwich trihydrides show a similar trend: the second-row systems [Cp₂NbH₃] and [Cp₂MoH₃]⁺ display exchange couplings, whereas their third-row Ta and W counterparts do not.³⁶ DFT calculations have modelled this behaviour, and shown it to be related to the stability of the dihydrogen-hydride form:³⁸ the higher energy and more diffuse 5d orbitals of Ta and W contribute to M–H bonds which are about 50% stronger than their 4d counterparts and hence stabilise the MH₃ form with respect to the M(H)(η^2 -H₂) alternative. Excellent reviews of tunnelling effects in these trihydride systems have been published by Sabo-Etienne and Chaudret,³⁶ and by Eisenstein *et al.*³⁸

In addition to trihydrides, some dihydrogen complexes show puzzling effects in their NMR spectra. For example, the system [Cp*Ru(dppm)(η^2 -H₂)]⁺ exhibits a temperature-dependent value of J_{HD} , which implies that the H...H distance in the dihydrogen moiety changes with temperature. A neutron-diffraction study of a salt of this cation gave $r_{\text{HH}} = 1.10$ Å, placing it in the regime of stretched dihydrogen complexes (Section 2.2).⁴² Quantum chemical calculations, supported by isotopic substitution studies, have confirmed that the H...H distance is indeed temperature-dependent. MH₂ moieties in stretched dihydrogen systems are characterised by very flat, anharmonic potential surfaces, and thermal population of low-lying excited vibrational states with large amplitude displacements has a significant effect on r_{HH} .³⁸

5 Overview

Section 1 reveals the chemistry and reactivity of classical TM hydrides to be remarkably varied and unconventional, and Sections 2–4 proceed to describe a wide spectrum of more unusual behaviour, across what appear to be three distinct and unrelated areas. As intimated in the Introduction, however, these peculiarities can all be traced back to a common origin: the unique electronic simplicity of hydrogen. As an element, hydrogen defies most attempts to force it into a Periodic

classification. Its single valence 1s orbital and absence of core electron density allow for uniquely close approach and good bonding overlap with many other atoms, whilst its remarkably high electronegativity – a consequence of these same electronic properties – is comparable with that of the majority of the TMs, resulting in a rich and diverse molecular chemistry for TM hydrides. The spherically symmetrical 1s orbital encounters minimal symmetry restrictions in typical reactions such as insertion and migration, as described in Scheme 1, and is well suited to indulge in the wide range of three-centre bonding interactions discussed in Section 2. The small size of the hydrogen atom, which necessitates no more than a single coordination site for σ -complexation of X–H bonds, also contributes to the wide spectrum of chemistry described in Section 2.

In addition to encouraging the formation of strong primary bonds, the lack of non-bonding electron density also facilitates remarkably strong secondary interactions of the type H...X – a feature apparent in the ubiquitous phenomenon of hydrogen bonding, which is displayed by molecular hydrides across the Periodic Table. Hydrogen-bonding interactions involving TM hydrides are discussed in Section 3, but strong secondary H...H interactions also play an important role in facilitating some of the quantum mechanical effects described in Section 4. For example, the so-called ‘*cis*-effect’, involving an apparent electrostatic attraction between the hydride and dihydrogen moieties in the complex [(PPh₂Et)₃FeH₂(η^2 -H₂)], was noted long before quantum mechanical exchange phenomena were appreciated in TM polyhydrides,³⁸ and was used to explain the facile exchange between M–H and M(η^2 -H₂) ligands. In a similar vein, so-called inter-ligand hypervalent interactions in TM silyl hydride complexes like [Cp₂NbH(SiMe₂Cl)₂] are considered by Nikonov to arise from interaction between a donor M–H moiety and a Lewis-acidic Si centre.⁴³

In summary, TM hydrides constitute a remarkable class of molecular complexes, which have appeared relatively late on the scene but which continue to pose structural and chemical conundrums. Their central involvement in catalysis and metal-mediated organic transformations maintains their position at the forefront of chemical research. Whilst their unusual behaviour can often be traced back to the unique and peculiar properties of hydrogen as an element, the link is not always clear-cut or direct.

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