

## The 2009 NZIC Presidential Address

# Magic Metals: The Special Affinity of Transition Metals for Hydrogen

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Thomas Graham, the first president of the Chemical Society (London) was a remarkable chemist who contributed in many ways to the development of the subject. However, perhaps his most remarkable discovery (though not the one for which he is best known) was that palladium, an unreactive precious metal, would absorb and release hydrogen gas under mild conditions. This observation was a prelude to the nickel-metal hydride (NiMH) battery technology that is widely used today and to the current interest in hydrogen storage in metal systems. Several years prior to Graham's discovery, William Grove had developed a fuel cell that relied on the interaction of hydrogen gas with platinum electrodes to generate an electric current. Both systems are evidence of the affinity of hydrogen for transition metals, and that affinity has been the basis of many scientific discoveries and valuable technologies since the mid-19<sup>th</sup> century. Today, there is interest and speculation around the prospects for a *Hydrogen Economy*, namely, an economy based on the use of hydrogen and hydrogen-rich materials as secondary fuels replacing hydrocarbons in key applications, notably transport.

The early experiments of Grove and Graham illustrate two of the key features of the interaction of transition metals and hydrogen: the ease with which the strong H–H bond is cleaved by many transition metals and, once present as discrete hydrogen atoms bound to the metal, the ease with which hydrogen moves over a metal surface or through a metal lattice. This behaviour results, in part, from the availability of *d*-orbitals on the transition metal and the spherical symmetry of the 1*s* bonding orbital of hydrogen. In this article some of the interesting chemical and technological consequences of this unique relationship are explored.

Hydrogen is the most abundant element in the universe and is 9<sup>th</sup> most abundant by weight in the earth's crust (including the oceans), or 5<sup>th</sup> by number of atoms, and it forms compounds with virtually all the elements of the Periodic Table except for the Noble Gases. The diatomic molecule, H<sub>2</sub>, is notable for the very strong single bond (435 kJ/mol), which makes molecular hydrogen rather unreactive unless there is a significant energy input to overcome the activation barrier. This is where the magic of transition metals comes in as they are able to reduce the activation barrier to negligible levels. A hydrogen molecule approaching a metal atom on the surface of a particle or in a metal complex is readily cleaved into two hydrogen atoms that may then go on to react further with other molecules in the environment. In the case of Graham's palladium experiment, the hydrogen atoms released on the surface of the metal are free to diffuse into the holes,

or interstices, in the metallic lattice. In Grove's fuel cell, the platinum atoms on the surface of the electrode cleave the hydrogen molecule and thereby assist in the formation of hydrogen cations, releasing an electron into the electrical circuit.

Significant though fuel cells and hydrogen storage are to modern society, they do not compare with the importance of catalysis involving hydrogen. The French chemist, Paul Sabatier first reported the catalytic hydrogenation of alkenes in 1897 and deservedly won the 1912 Nobel Prize in chemistry for his discovery. However, it was William Norman who developed the first commercial process, the nickel-catalysed hydrogenation of vegetable oils to make fats, which were of more value than oils at that time. Norman's was the first of many chemical processes to employ a metal to lower the activation energy of reactions involving molecular hydrogen and hydrogen-containing molecules to the extent that metal-hydrogen catalysis provides the technological basis of much of the chemical industry.

The hydrogenation of vegetable oils is a relatively non-demanding application of transition metal catalysis as it employs small metal particles that are easily manufactured. However, much more sophisticated reactions are now possible, including the stereospecific hydrogenation of prochiral alkenes to generate molecules of a single chirality. This reaction has enormous potential significance, for example, in the pharmaceutical industry as recognized in 2001 by the award of the Chemistry Nobel Prize to William Knowles and Ryoji Noyori (jointly with Barry Sharpless) for the discovery of catalyst complexes that would induce chirality in the products of their reactions.<sup>1</sup> The Knowles and Noyori successes depend upon using other ligands bound to the transition metal to create a hydrogenation reaction site of the correct shape to produce the desired enantiomer. Knowles' work led to the industrial synthesis of the chiral drug L-DOPA used in the treatment of Parkinson's disease. Molecular (or homogeneous) catalysts can be designed in this way, but the approach would be impossible with the basic metal particle (heterogeneous) catalysts used by Norman and still widely used in routine hydrogenation reactions.

Amongst the many significant catalytic reactions involving hydrogen and transition metals (or their compounds) as catalysts is the synthesis of ammonia, developed by Haber and Bosch in 1909, that provides the feedstock for the fertilizer, explosives and parts of the synthetic fibre industries. This process is reckoned to provide food for one third of the world's population through the use of nitrogen fertilizers. There is also the 1926 Fischer-Tropsch process that converts a mixture of CO and H<sub>2</sub> (synthesis

gas) into liquid fuels and other chemical feedstocks. The South African SASOL Company developed this process to a level of sophistication during the period of economic isolation associated with the apartheid era in that country. A further application of synthesis gas is in the hydroformylation reaction discovered by Otto Roelen in the 1930s. This process can be employed to convert terminal alkenes into either aldehydes or alcohols from the addition of a formyl group (CHO) and a hydrogen atom to a carbon-carbon double bond. It differs from the Haber-Bosch and Fischer-Tropsch processes in that the catalyst is a discrete metal complex in the same phase as the reactants, *viz.* a homogeneous catalyst, rather than a metal-containing, heterogeneous solid catalyst. In this respect the hydroformylation catalyst resembles the hydrogenation catalysts developed by Knowles and Noyori.

Hydrogen gas is produced in NZ on a significant scale as a key material in several industrially important processes. Methanex NZ operates two plants in Taranaki that convert methane into methanol in a process that first combines CH<sub>4</sub> and H<sub>2</sub>O to give synthesis gas, and then recombines the CO and H<sub>2</sub> affording methanol. Over 90% of the methanol is exported and the plants are operated flexibly to meet international demand. Typical recent production is in the region of 2500 tonnes per day, but it varies according to international demand and the availability of methane; a nickel catalyst is used in the production of methanol.

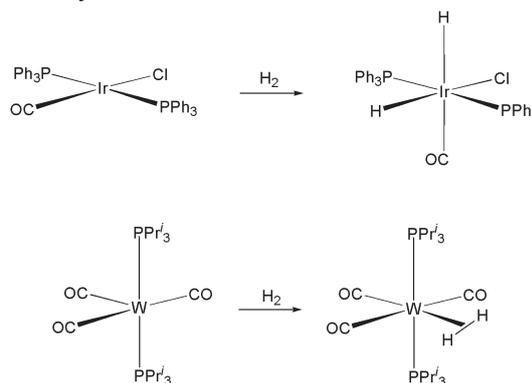
New Zealand's agricultural economy is heavily dependent on the judicious use of nitrogen fertilizers to promote grass growth. Some of that nitrogenous fertilizer is supplied by the Balance Agri-Nutrients ammonia-urea plant at Kapuni, also in Taranaki. The ammonia is produced from synthesis gas by the Haber-Bosch catalytic process. Much of the ammonia is then converted to urea for agricultural applications. A third major producer of hydrogen in NZ is the oil refinery at Marsden Point. Once again some of the key processes in petroleum refining depend for their operation on the interaction of hydrogen with transition metals.

Having established the economic importance of the interaction of hydrogen and transition metals, one should ask what is known about the fundamental nature of the interaction of hydrogen and transition metals. There has been detailed study of that interaction both with the surface of bulk metals and with metal centres in discrete metal complexes. However, there appears to be no fundamental difference in the nature of the interactions, although the environments are clearly different. As it is generally true that a wider range of experimental techniques can be brought to bear on metal complexes, the remainder of this article is focused in that direction.

All transition metals form complexes with hydrogen in which individual hydrogen atoms are covalently bound to one or more transition metals. As the electronegativity of hydrogen is similar to that of many transition metals, the bonds are not very polar and they rarely display ionic character. Although there are examples of both classical acidic or hydridic (the tendency of transition metal hy-

dride complexes to behave as true hydrides) behaviour by individual complexes, these are not the predominant reactivity patterns of hydride complexes.

The first hydride complexes were reported by Walter Hieber in the 1930s, but interest in them expanded only in the 1950s. This was in parallel with the rapid growth of transition metal organometallic chemistry and the development of instrumental techniques particularly suited to the identification of hydride ligands, *e.g.* IR and NMR spectroscopies. Whereas there are only a few examples of complexes such as the remarkable [ReH<sub>9</sub>]<sup>2-</sup>, in which the metal is stabilized only by hydride ligands, there are many hydride complexes that contain other ligands that are often influential in dictating the chemical behaviour of the hydride ligands themselves. There are many ways of synthesising transition metal hydride complexes, including direct reaction with hydrogen gas. A landmark paper in the area, published in 1962 by Vaska and DiLuzio,<sup>2</sup> described the reaction of molecular hydrogen with an iridium complex [IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>]. Under mild conditions, the very strong H–H single bond (435 kJ/mol) is broken and two discrete hydride ligands are formed (Scheme 1). This reaction provides a model for the key step in the catalytic hydrogenation reaction discovered many years earlier by Sabatier.



Scheme 1. Contrasting interactions of H<sub>2</sub> with transition metal complexes.

Twenty years later Kubas *et al.*<sup>3</sup> provided a further insight into this critical reaction when they reacted hydrogen gas with the tungsten complex [W(CO)<sub>3</sub>{P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>}<sub>2</sub>] and isolated a complex of *molecular* hydrogen, *i.e.* a complex in which the single bond of the H<sub>2</sub> molecule was not fully broken by interaction with the metal (Scheme 1). Not only did this provide evidence for the mechanism of H–H bond cleavage by transition metals but it also forced transition metal chemists to rethink their ideas of the metal–ligand bond that had been ingrained over many years. In the classical view, the metal is a Lewis acid with a vacant orbital and the ligand is a Lewis base with a pair of non-bonding electrons that can be *donated* to the metal orbital. Thus, molecules like NH<sub>3</sub> or PPh<sub>3</sub> that have lone pairs on N and P, respectively, are excellent ligands for transition metal complexes. With the development of transition metal organometallic chemistry, chemists had to broaden the definition of *donor electrons* to include the high-energy  $\pi$  electrons in unsaturated molecules such as ethene. However, in Kubas' molecular hydrogen compound, it is the very stable electrons in the H–H  $\sigma$  bond that are act-

ing as the donor electrons. An understanding of the way transition metals interact with the H–H  $\sigma$  bond, and other  $\sigma$  bonds in molecules such as methane, is likely to have a profound effect on the development of catalysis in the future.

We have been interested in the structure and reactivity of *polyhydrides*, complexes with large numbers of hydride ligands and close relatives of  $[\text{ReH}_9]^{2-}$ . Some years ago, in collaboration with Professor Judith Howard,<sup>4</sup> we established that the structure of the osmium polyhydride  $[\text{OsH}_6(\text{PPr}^i_2\text{Ph})_2]$  was a distorted triangular dodecahedron with six discrete hydride ligands. More recently,<sup>5</sup> we investigated the reactions of these molecules with acids and were able to identify an unstable cationic intermediate  $[\text{OsH}_7(\text{PPr}^i_2\text{Ph})_2]^+$ . What structure did this complex have? We suspected that some of the hydrogen atoms might be bonded together as coordinated  $\text{H}_2$  molecules in a way similar to that in Kubas' compound, but how could that be established? The proton NMR spectrum showed only one signal for all seven hydride ligands. As these cannot be equivalent, the signal merely indicates that there are very low energy barriers to internal molecular rearrangement and that all seven hydrogens exchange positions rapidly on the NMR timescale. Single crystal neutron diffraction is the definitive technique for establishing the structure of hydride complexes involving heavy atoms such as osmium. However, neutron diffraction requires relatively large stable crystals and these were not available in this case. We chose, therefore, to use a technique that had been developed by Crabtree<sup>6</sup> and others to identify the presence of close H–H contacts – the NMR relaxation parameter,  $T_1$ . This parameter is highly dependent on the closeness of the hydrogens, so that a typical value for  $T_1$  in a classical transition metal hydride (where hydride ligands may be  $>170$  pm apart) is 300 ms. Fig. 1 shows the measured value of  $T_1$  for  $[\text{OsH}_7(\text{PPr}^i_2\text{Ph})_2]^+$  at various temperatures and the extrapolated minimum value of approximately 18 ms is good evidence that the complex should be correctly formulated as  $[\text{OsH}_5(\text{H}_2)(\text{PPr}^i_2\text{Ph})_2]^+$  or even  $[\text{OsH}_3(\text{H}_2)_2(\text{PPr}^i_2\text{Ph})_2]^+$  with one or two molecular hydrogen ligands respectively.<sup>5</sup>

Of course molecular hydrogen is an excellent leaving group as the interaction between the metal and the H–H  $\sigma$  bond is relatively weak. It is no surprise, therefore, that  $[\text{OsH}_7(\text{PPr}^i_2\text{Ph})_2]^+$  decomposes readily at room temperature to form the diosmium complex  $[\text{Os}_2\text{H}_7(\text{PPr}^i_2\text{Ph})_4]^+$  with loss of  $\text{H}_2$ . Complexes or clusters with several metal atoms and multiple hydride ligands are fascinating molecules and are not uncommon. As our example illustrates, the hydrogen atom, with only a single  $\sigma$ -orbital for bonding, will, nevertheless, interact strongly with two or more transition metals. Another interesting feature of molecules of this type is that the hydrogen atoms are often very mobile and, unlike the hydrogen atoms in organic molecules, they will readily exchange positions in the structure. The hydrogen atoms in transition metal clusters are frequently chemically reactive, and because the metal-metal bonds ensure the integrity of the cluster, hydrogen can often be added and removed reversibly.<sup>7</sup> An example<sup>8</sup> is the platinum cluster  $[\text{Pt}_4(\text{PBu}^t_3)_4\text{H}_7]^+$  that is readily oxidized,

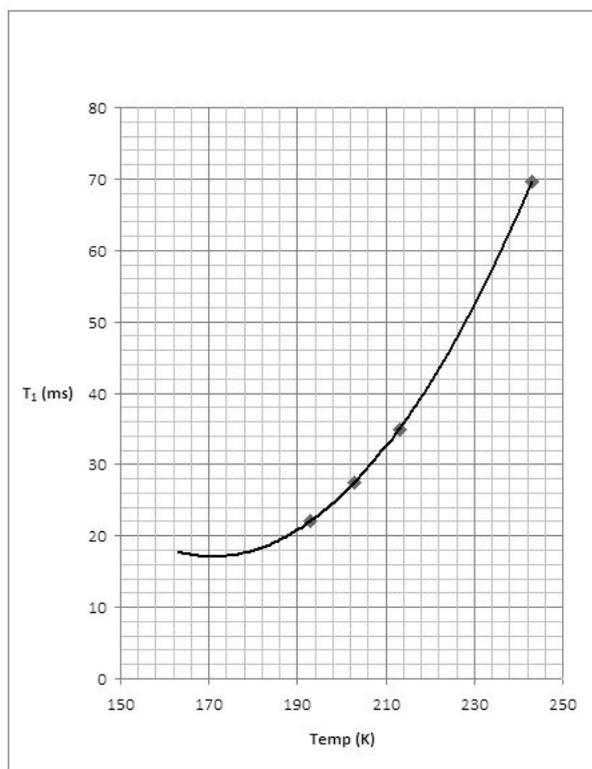
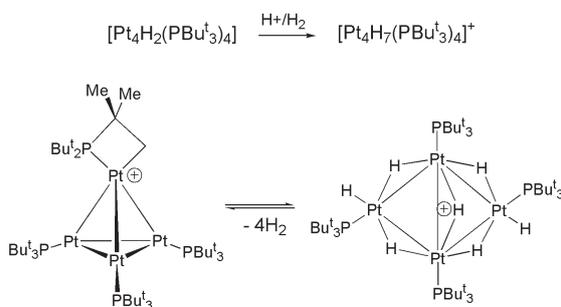


Fig. 1. Spin-lattice relaxation time,  $T_1$  for  $[\text{OsH}_7(\text{PPr}^i_2\text{Ph})_2]^+$  measured at low temperature (300 MHz,  $\text{CD}_2\text{Cl}_2$ ).

losing four molecules of  $\text{H}_2$ , to afford  $[\text{Pt}_4(\text{PBu}^t_2\text{CMe}_2\text{CH}_2)(\text{PBu}^t_3)_3]^+$  (Scheme 2). The original cluster is readily regenerated under mild conditions by exposing the sample to hydrogen and it is the molecular analogue of Graham's reversible reaction of hydrogen with palladium metal.



Scheme 2. Reversible uptake of  $\text{H}_2$  by a transition metal cluster.

Although this may seem to be a rather specialized piece of research, the important point it illustrates is that transition metals allow the very fast formation and cleavage of strong  $\sigma$  bonds. A logical extension of the concept is to the catalytic cleavage or activation of the inert C–H bonds in alkanes, such as methane. Methane resources are enormous but its conversion into more useful feedstocks for the chemical industry is not a very efficient process, as the methane to methanol example mentioned above illustrates. With current technology, it is necessary to first convert  $\text{CH}_4$  and  $\text{H}_2\text{O}$  into  $\text{CO}$  and  $\text{H}_2$  before reassembling the synthesis gas into methanol. Although this is a mature technology and can be implemented on a very large scale, the process requires high temperatures and, for that reason, it is not energy efficient. A more elegant synthesis would cleave a single C–H bond leaving a  $\text{CH}_3$  group intact. A major goal of organometallic chemistry is the

catalytic activation of C–H bonds under mild conditions. If that is ever achieved then the energetics of the process will be driven by the strong bonds that form between transition metals and hydrogen and by the facility with which transition metals interact with  $\sigma$  bonds.

The race to develop new energy technologies to replace oil has led to a renewed interest in the ability of transition metals to interact with hydrogen and hydrogen-containing compounds. A particular issue is the storage and release of hydrogen. Unfortunately, the platinum clusters given as examples above cannot form the basis of a workable commercial hydrogen storage system simply because of the cost and rarity of platinum, and the modest storage capacity involved. However, the original work of Graham that demonstrated the ability of palladium to absorb large quantities of hydrogen gas under mild conditions was a precursor of modern NiMH battery technology that now is widely used in hybrid cars and was previously common in laptop computers until it was displaced by lithium ion batteries that have a better energy-to-weight ratio. In NiMH batteries, hydrogen is electrochemically generated during recharging and stored in the interstices of an  $AB_5$  alloy of a lanthanide metal (A) and a transition metal (B). To meet the power demands of rapid acceleration in a hybrid car, hydrogen must be able to diffuse rapidly through the metallic lattice and be released easily for oxidation at the anode. Unfortunately, as with most battery technologies, the low energy-to-weight ratio of NiMH batteries means that they will never be a direct replacement for the internal combustion engine.

Fuel cells that rely on hydrogen or a hydrogen-rich fuel are a potential replacement for the petrol engine in transport. Many fuel cell designs depend on a platinum activated electrode, just as the original Grove cell of 1842 did. However, platinum is a rare and expensive element and it is questionable whether there is enough in the earth's crust for all the fuel cells that might be required for the *hydrogen economy*. The search is on for cheaper replacements for platinum as the electrode material. However, a much greater problem preventing the adoption of the hydrogen fuel cell is the lack of a convenient reversible method of storing hydrogen. As pointed out above, the  $AB_5$  alloys are too heavy to be practical. Light metals such as magnesium will store large quantities of hydrogen but the lack of *d*-orbitals means that the activation barriers

for absorption and release of hydrogen are high. The non-metallic hydrides such as those of boron and nitrogen, and even carbon itself, are very attractive on grounds of high energy density. But once again the activation barriers and thermodynamic parameters are unfavourable. Transition metal catalysts, and in particular those made from the cheaper and more abundant metals, are strong candidates to lower the activation barriers to acceptable levels. With careful design, this could lead to a light atom hydrogen storage system where the energy differences and activation barriers between the hydrogenated and dehydrogenated forms are relatively low; it could thus form the basis of a practical hydrogen economy. Transition metals are also likely to have a significant role in the development of technologies for the renewable production of hydrogen from sunlight.<sup>9</sup>

Despite the long scientific and technological history of the interaction of transition metals with hydrogen, it is likely that many important discoveries are still to be made, and new technologies will be developed. Transition metals lower activation barriers for reactions that involve hydrogen and hydrogen-containing compounds. Because of this, it is probable that they will play a critical role in the development of technologies to reduce the energy requirements of the chemical industry, and provide working solutions to the problem of finding an alternative to fossil fuels.

## References

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