Heterobimetallic complexes: A unique H_2-activating catalyst and a model for hydrogenase

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The activation of hydrogen to give two protons and two electrons is a very crucial process for the generation of electricity in fuel cells. It has been known for a long time that enzymes called hydrogenases in anaerobic bacteria strip the hydrogen into protons and electrons for production of energy. However, the mechanistic aspects of the activity remains undocumented because of the complexity of the enzymatic processes. This led researchers to investigate the mechanism of hydrogen splitting using model compounds. In addition to using H_2 to carry out the reductions, the model must have high thermodynamic efficiency.

The late 1970s experienced a flurry of interest in transition metal homonuclear bimetallic complexes because of their potential applications in catalysis. Following this, considerable attention was focused on the chemistry of complexes containing divergent transition metal centres[1–3]. It has been suggested that the two metal centres could act in a cooperative fashion to activate small molecular substrates[4]. The potential use of heterobimetallic complexes in reduction processes depends on the ability to incorporate hydrogen presumably as hydride ligands.

Barring the report by Halpern and coworkers[5] more than three decades ago on the activation of hydrogen homogeneously in which H_2 is used as a source of electrons, there have been no extensive studies in this field. It was found that the chloride complexes of Ru^{III} in aqueous HCl solution under mild conditions, catalyses the homogeneous reduction by hydrogen of Ru^{IV} and of Fe^{III}. The Ni–Fe hydrogenase from *Desulfovibrio gigas* contains a nickel centre which is considered the active site and three *Fe–S centres*, two [4Fe–4S]$^{2+,1+}$, and one [3Fe–4S]$^{1+,0}$ clusters[6]. Because of the difficulty in synthesizing models containing Ni–Fe due to their similar chemical reactivity, recently Hembre and coworkers have resorted to using Ru–Fe, widely different chemically, in their model complexes to study hydrogen reduction[7].

The synthetic model, a heterobimetallic complex, Cp*(dppf)RuH (Cp* = pentamethylcyclopentadienyl, dppf = 1,1′-bis(diphenylphosphino ferrocene)), was prepared by slight modification of the literature procedures[8] involving reaction of a benzene solution of $[Cp^*RuCl_2]_n$ with dppf in the presence of zinc. The treatment of the resulting Cp*(dppf)RuCl with NaOMe gave the hydride complex in good yield (87%) as an orange powder. A second method has also been established, albeit in lower yields for Cp*(dppf)RuH wherein dppf displaces PPh_3 from $Cp^*Ru(PPh_3)_2Cl$ followed by reaction with NaOMe. Suitable crystals were obtained from benzene–methanol solution. In addition to the spectroscopic and the elemental analysis data, the molecular structure of the heterobimetallic hydride complex was determined by X-ray crystallography and shown in Figure 1.

In comparison to somewhat analogous 'three-legged piano-stool' derivatives of the type $CpRu(PR_3)_2X$ (ref. 9), there exists no unusual feature in the Cp*(dppf)RuH complex. However, the steric crowding of the Cp* moiety is nicely demonstrated in this complex in comparison to the Cp analog, which was reported by Bruce and coworkers[10]; the hydride ligand was not located crystallographically in Bruce's complex. Because of the steric bulk of the Cp* ligand, compression of the phenyl groups of dppf takes place resulting in their flattened orientations. Due to this flattening, a small hydrophobic pocket around the hydride is formed by one of the adjacent phenyl rings. This is not seen in the unsubstituted Cp analog. In the case of $CpRu(PPh_3)_2H$, the hydride ligand is effectively shielded by the PPh_3 ligands against attack by bulky external reagents[11]. Cp*(dppf)RuH is

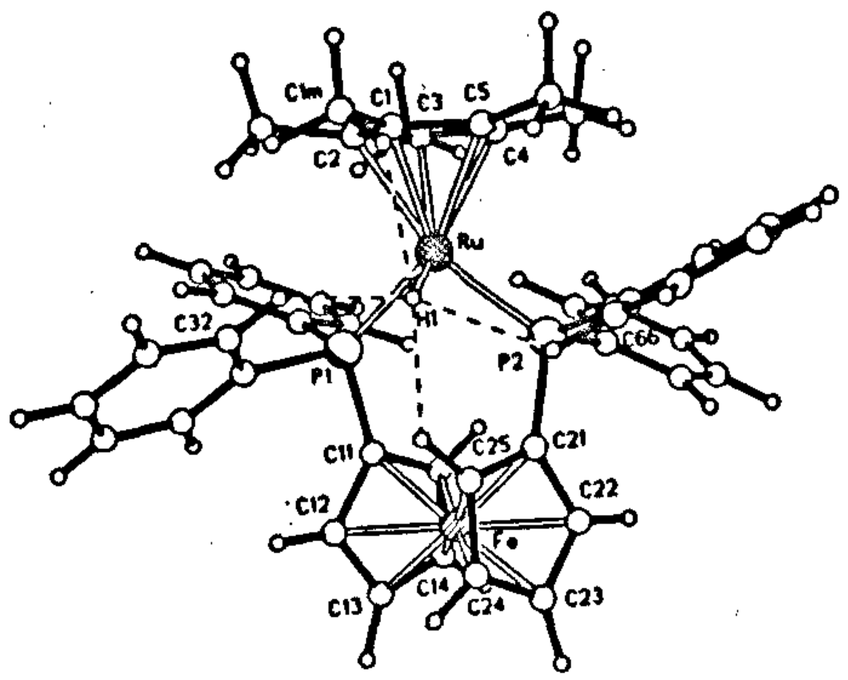

Figure 1. Molecular structure of Cp*Ru(dppf)H.

$$H_2 + 2TMP + [Cp_2Fe]PF_6 \xrightarrow[THF]{Cp^*(dppf)RuH(1\%)} Cp_2Fe + 2[TMPH]PF_6$$
(or MV^{2+}) (or MV^{+})

Scheme 1.

one of few three-legged piano-stool type hydride systems[9,12,13] that has been completely structurally characterized.

The Hembre group studied the electrochemical oxidation of their model complex by cyclic voltammetry and found that the process was reversible! In presence of electron acceptors such as ferrocinium ion or methyl viologen (MV^{2+}), the complex releases an electron resulting in a 17-electron stable, isolable hydride cation which can be reduced back to its parent hydride by cobaltocene. The researchers found that ferrocinium ion or methyl viologen (MV^{2+}) can also be reduced by H_2 in the presence of a base (tetramethyl piperidine) and a catalytic amount of their model complex. Their studies show that the splitting of H_2 into electrons and protons takes place as follows: a proton is released once H_2 is bound to Ru followed by transfer of electrons of H_2 to electron acceptors mediated by the metal and finally the release of the remaining proton (Scheme 1).

They refer to their system as a 'redox switch' catalyst because the Fe–Ru model acts as a template for the conversion of a two-electron reducing agent, H_2, into one-electron equivalents in a catalytic manner (8.5 turnovers/min at ambient temperature and pressure) mimicing the hydrogenase enzyme.

Hembre's Cp*(dppf)RuH is the first example of the hydrogenase model complex that has hydrogen-splitting ability. Fuel cells are the subject of a great deal of research, and may in the future be used as sources of industrial and domestic electricity. Service[14] predicts that if Hembre's compounds perform just as efficiently as platinum catalysts, ruthenium, a much cheaper metal may as well replace Pt from fuel cells, thus reducing the cost and making them good model power sources. We can anticipate further new developments in this direction especially incorporating much less expensive metals in the models but having close resemblance to the real protein in terms of its activity.

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Metallization of hydrogen – Everest conquered?

One of the dreams of the condensed matter physicist, of making the element hydrogen into a metal seems to have been achieved by a group led by W. J. Nellis, who has been working on this problem for some time. S. T. Weir, A. C. Mitchell and W. J. Nellis of the Lawrence Livermore National Laboratory in an article in the March issue of *Physical Review Letters* (1996, **76**, 1860) have claimed having produced metallic hydrogen. For more than six decades scientists have been speculating and theorists have been predicting the metallization of hydrogen. But this simplest of elements has ignored the theorists and has resisted becoming a metal for a long time; and when it did, the transformation was from the liquid state and not from the solid state as predicted. Further it took place at temperatures and pressures very different from those expected!

There are two routes to obtain high pressures. The first is to create very high static pressures in a diamond anvil cell (see *Curr. Sci.*, 1991, **61**, 710) in which pressures in the range 2.5 megabars have been achieved. The second route, the one taken by the Lawrence Livermore group, is by a high pressure shockwave produced by a hypervelocity impactor fired from a two-stage gas gun. In the final experiments reported, the impactor, a 25 mm disc struck the front face of an aluminium sample holder at a speed of 7.33 km/s. The sample holder contained a thin layer (0.5 mm), liquid hydrogen (or liquid deuterium) sandwiched between two insulating sapphire anvils (see Figure 1). The shock wave passes through the anvils into the hydrogen, reverberates between the anvils and builds up pressures of 93–180 gigapascals (or megabars). The temperature too rises but the cryogenic system keeps it down to between 2200–4400 K, which is low enough to prevent the hydrogen molecule from dissociating. The high pressures are reached within 10^{-9} seconds of the impact and persist for almost 500 nanoseconds giving sufficient time for the fast electronic system to measure the resistivity of the sample.

The resistivity is measured through 1 mm electrodes inserted through the