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Activation of dihydrogen and coordination of molecular H_2 on transition metals

Gregory J. Kubas*

Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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ABSTRACT

Fifty years ago, when this journal was founded, organometallic chemists could not have imagined that common small molecules such as dinitrogen and especially dihydrogen could function as ligands. Dihydrogen has long been vital in catalytic processes such as hydrogenation and conversions of organic compounds and is now being considered as a future energy storage medium. Dihydrogen is only useful chemically when the two strongly bound H atoms are split apart in a controlled fashion. Although metal hydrides were first well established in 1955, the structure and mechanism by which H_2 binds to and undergoes cleavage on transition metals was not ascertained until even more recently in the history of inorganometallic chemistry, about 20 years after this journal was first published. The activation of dihydrogen is a fascinating saga that has slowly unfolded over the past 80+ years, as will be chronicled in this Perspective. There is a marvelous analogy between the metal-olefin π bonding model first brought to light by Dewar, Chatt, and Duncanson 60 years ago and the bonding model for side-on σ-bond coordination discovered by us 30 years ago. There are two separate pathways for H–H (and X–H σ-bond activation in general) that directly depend on the electronics of the metal σ-ligand bonding. Metal *d* to σ^* X–H backdonation is the key to stabilizing σ-bond coordination and also is crucial to its homolytic cleavage (oxidation addition). For electrophilic complexes, particularly cationic systems with minimal backdonation, heterolytic cleavage of H_2 is common and is a key reaction in industrial and biological catalysis.

1. Introduction to the activation of dihydrogen and other σ-bonds

1.1. Historical perspectives

Fifty years ago, when this journal was founded, organometallic chemists could not have imagined that common small molecules such as dinitrogen, dihydrogen and, least of all, methane could function as ligands. Indeed such saturated molecules along with noble gases were long utilized as inert atmospheres for conversions of highly reactive or air sensitive compounds. In the context of this article, dihydrogen (H_2) has long been vital in catalytic processes such as hydrogenation and conversions of organic compounds. It is also being considered as a future energy storage medium, with hydrogen production and storage at the forefronts of research. Dihydrogen, being held together by a strong two-electron H–H bond, is only useful chemically when the two H atoms are split apart in a controlled fashion. Metal hydrides were actually not well characterized until 1955, surprisingly late in the history of inorganometallic chemistry. The structure and mechanism by which H_2 binds to and undergoes cleavage on transition metals was not ascertained until even more recently, almost exactly 20 years after this journal was first published in October, 1963.

The activation of dihydrogen is a fascinating saga that has slowly unfolded over the past 80+ years and was often frustrated by the clandestine nature of diminutive (and often highly dynamic) hydrogen atoms and molecules in the coordination sphere of much more massive transition metals. There is strong relation here to the half-century old quest to understand the even more complex structures and mechanisms of enzymes such as nitrogenase and hydrogenase, which at the molecular level remain some of the most baffling mysteries in all of science. Tantalizing pieces of the puzzles are revealed over time, while at the heart lies a common denominator: exactly how very strongly bonded diatomic molecules like H_2 and N_2 split and become chemically transformed on metal centers.

As is often the case, the reactivity of these small molecules on transition metal centers preceded structural, spectroscopic, and

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* Tel.: +1 505 466 3907.
E-mail address: gkubas1@comcast.net.

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mechanistic information. As a consummate example, both heterogeneous and homogeneous catalytic hydrogenations were established long before even the simplest metal hydride complexes were definitively characterized. This is shown in the timeline (Fig. 1) that depicts many of the significant events that are relevant to this perspective.

Many reviews have been published on this subject, and a retrospective account of homogenous catalytic hydrogenation was published in 1980 by a pioneer in the field, Jack Halpern [1]. He points out that Brian James' 1973 monograph, "Homogeneous Hydrogenation," [2a] cites nearly 2000 references during the preceding 20 years. However, only two documented examples of homogeneous catalytic activation of H_2 by metal complexes were reported prior to 1953 when Halpern began his studies and heterogeneous hydrogenation predominated. The first dates back to 1938 when Calvin reported that Cu(I) salts such as Cu(I) acetate catalyzed reduction by H_2 of substrates such as Cu(II) and quinone under mild homogeneous conditions [3]. Surprisingly this discovery was not well recognized or even followed up for fifteen years. Halpern commented that activation of H_2 had long been attributed to the distinctive properties of solid surfaces, implying that H_2 had originally been thought to be unreactive with metal complexes in solution. This was understandable considering that the first transition metal hydride complex, $H_2Fe(CO)_4$, was not discovered until 1931 by Hieber, and his claim of a covalent M–H bond remained controversial for many years afterward! [4]. Surprisingly, only beginning around 1955 did M–H bonds become better characterized and generally accepted when Wilkinson determined the IR and NMR spectra of Cp_2ReH. This complex was significant also in that it could be easily protonated because the M–H bond is as basic as ammonia (Eq (1)).

$$Cp_2ReH + H^+ \rightarrow [Cp_2ReH_2]^+ \qquad (1)$$

Here the product is a classical dihydride, but as will be shown this is now a common route to nonclassical molecular hydrogen complexes, the major subject of this article. It was not until 1960 and ensuing years that the first crystal structures of transition metal hydrides were determined, although the hydride positions could not be located. The first complex for which the hydride ligand was found crystallographically was for $RhH(CO)(PPh_3)_3$ prepared by Vaska and Bath [5]. The structure was reported by La Placa and Ibers in 1963 [6], the same year this journal was founded, and showed that the Rh–H distance was 1.72(15) Å. This was an important finding because this distance was "normal" as judged by the usual radii sum rules and not abnormally short (<1.2 Å), as was the subject of early speculation. The first neutron structure of a transition metal hydride was determined by Kerro Knox in 1964 for the Re polyhydride, $[ReH_9]^{2-}$ [7]. Interestingly this was performed at Case Institute of Technology while I was an undergraduate there, although I did not realize the significance of hydride chemistry at the time. Twenty seven years later, it was found that substituting two hydrides by two phosphines gave a neutral complex with a "stretched" dihydrogen ligand, the first example of its kind as will be discussed below.

The second homogeneous catalytic system, discovered by Roelen [8] also in 1938, involved hydrogenations catalyzed by cobalt carbonyl complexes, particularly hydroformylation of olefins. The latter is also called the oxo process and is exemplified in Eq (2).

$$RCH = CH + H_2 + CO \xrightarrow{[Co_2(CO)_8]} RCH_2CH_2C(=O)H \qquad (2)$$

This immensely important industrial reaction, which marks its 75 anniversary this year [9], now primarily utilizes rhodium phosphine complexes as catalysts.

Starting in the late 1950's, considerable debate existed about how H_2 interacted with a metal center as the initial step in H–H cleavage in processes such as the above. Some researchers believed H_2 would act as a Lewis base, i.e. σ donation to a vacant metal *d* orbital, and some viewed H_2 as a Lewis acid, accepting electrons from a filled metal orbital into the σ* orbital (end-on bonded H_2, Scheme 1).

In 1959 both Halpern [10] and Syrkin [11] speculated that activation of H_2 involved attack of the bonding electrons of H_2 on a vacant metal *d* orbital via a three-center transition state as above (η^2-H_2). Other researchers believed the opposite: transfer of electrons from an occupied *d* orbital to the antibonding (σ*) orbital of η^1-H_2 [12–14]. However, these constructs were generally thought

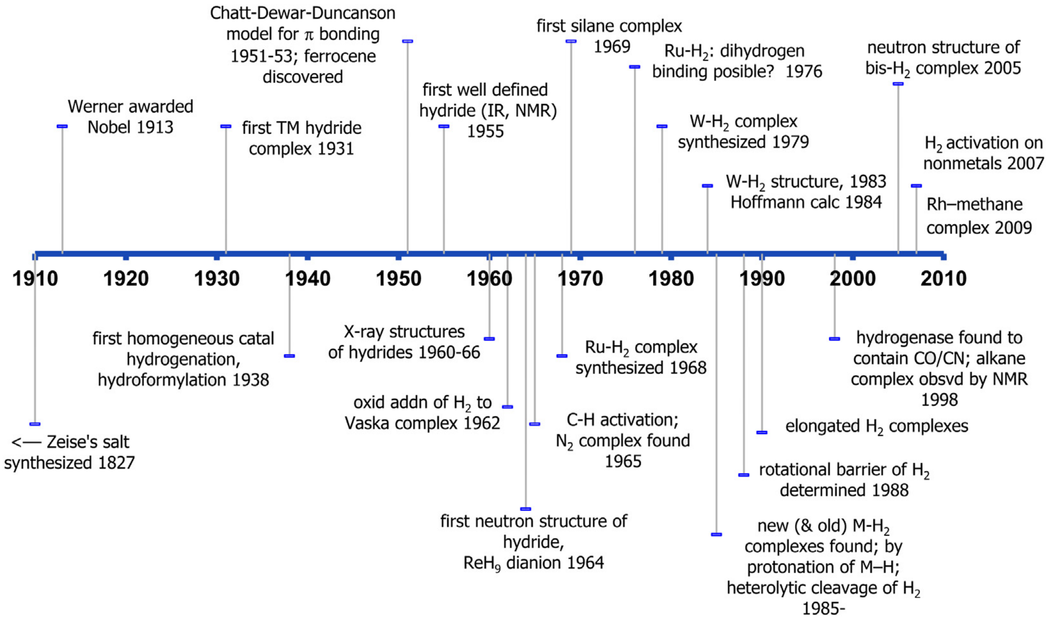

Fig. 1. Timeline for coordination and activation of dihydrogen and other small molecules.