

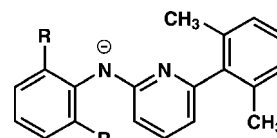
# Dihydrogen-Catalyzed Reversible Carbon–Hydrogen and Nitrogen–Hydrogen Bond Formation in Organometallic Iridium Complexes\*\*

José E. V. Valpuesta, Nuria Rendón, Joaquín López-Serrano, Manuel L. Poveda, Luis Sánchez, Eleuterio Álvarez, and Ernesto Carmona\*

The molecule dihydrogen plays a key role in nature.<sup>[1]</sup> Although in recent times it has become the ideal energy carrier,<sup>[2]</sup> its generation in vast quantities by environmentally clean methods is still a major scientific and technical challenge.<sup>[3]</sup> Nonetheless, H<sub>2</sub> is an essential reagent for many highly important heterogeneous and catalytic processes.<sup>[4]</sup>

Homogeneous hydrogenations were originally thought to entail oxidative addition and reductive elimination at a metal center,<sup>[4b]</sup> but the pioneer discovery by Kubas and co-workers of the first sigma-complex of H<sub>2</sub><sup>[5]</sup> led to a new paradigm that emphasizes the key role of such species in this and other transformations.<sup>[6,7]</sup> Direct hydrogen transfer from metal–H<sub>2</sub> complexes may occur, an important step in catalytic hydrogenations by electrophilic compounds being heterolytic H<sub>2</sub> activation.<sup>[8]</sup> H–H heterolysis is relevant to the function of hydrogenases<sup>[9–13]</sup> and may proceed intramolecularly, with formal proton transfer to a *cis* sulfur, nitrogen, or oxygen donor ligand.<sup>[12,9,14–16]</sup> In the last years, activation of dihydrogen by compounds of main-group elements has also been demonstrated.<sup>[17,18]</sup>

In view of the myriad of stoichiometric and catalytic hydrogenations known, it is plausible that in addition to being a key reagent, the molecule of H<sub>2</sub> could act as a catalyst of important transformations such as the formation and cleavage of H–X bonds in coordination compounds (where X represents for example C, O, N, or S). However, while commonly used ligands, such as N-heterocyclic carbenes, have been shown to catalyze sophisticated organometallic rearrangements,<sup>[19]</sup> information on catalysis by H<sub>2</sub> is scarce,<sup>[20]</sup> and to our knowledge it has never been disclosed in a homogeneous system. Herein we show that H<sub>2</sub> catalyzes with high efficiency the formation and rupture of C–H and N–H bonds of iridium-

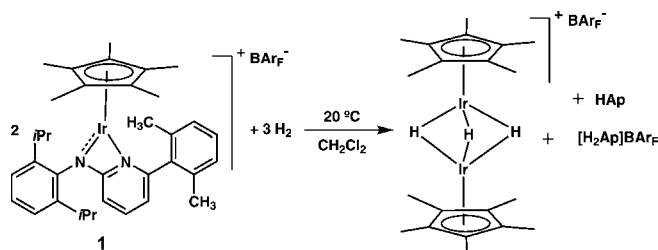


**Scheme 1.** The anionic aminopyridinate ligands employed in this work (R = *i*Pr, complexes **1** and **2**; R = CH<sub>3</sub>, compounds **3** and **4**).

bound aminopyridinate ligands (Scheme 1) in an organometallic system.

Similarly to somewhat related complexes,<sup>[12,21]</sup> the aminopyridinate iridium compound **1** (Scheme 2) that contains an {( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ir<sup>III</sup>} unit and an aminopyridinate group in which the amido functionality acts as a  $\sigma$ - and  $\pi$ -donor ligand, reacted with H<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>, 1 atm) to yield a known dinuclear trihydride,<sup>[22]</sup> along with an equimolecular mixture of the free and protonated aminopyridine, HAp and [H<sub>2</sub>Ap]BAR<sub>F</sub>, respectively (BAR<sub>F</sub><sup>−</sup> = B[3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>4</sub><sup>−</sup>). Before reaching completion, NMR studies of the reaction mixture revealed the presence of small amounts of unreacted **1** and of a third metal-containing product, **2**, which was subsequently isolated and characterized as an isomer of **1** with the structure shown in Figure 1. As can be seen, formation of complex **2** requires activation of a benzylic C–H bond of **1**, with formal hydrogen transfer to the amido nitrogen. An eighteen-electron configuration is achieved in the latter species by means of pseudoallylic coordination of the activated benzylic unit.

Complexes **1** and **2** have been characterized by single crystal X-ray diffraction (Figure 1 B). In solution they exhibit characteristic <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra that are in accord with their structures (see the Supporting Information). Thus, whereas in **1** the two methyl groups of the pyridine aryl substituent (namely 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) appear in the <sup>1</sup>H NMR spectrum as a singlet with  $\delta$  2.28 ppm (relative intensity 6H), in isomer **2** this signal is replaced by a singlet at 2.48 ppm (3H) plus two doublets at 3.68 (1H) and 2.07 (1H) ppm (<sup>2</sup>J<sub>HH</sub> = 4.5 Hz). The latter two signals are due to the Ir–CH<sub>2</sub> protons. Furthermore, a new signal attributable to the NH

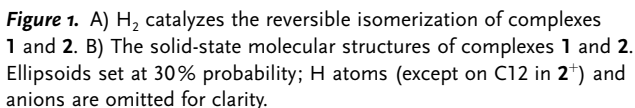


**Scheme 2.** Reaction of compound **1** with an excess of hydrogen.

[\*] Dr. J. E. V. Valpuesta, Dr. N. Rendón, Dr. J. López-Serrano, Prof. M. L. Poveda, Dr. L. Sánchez, Dr. E. Álvarez, Prof. E. Carmona Departamento de Química Inorgánica-Instituto de Investigaciones Químicas (IIQ), Universidad de Sevilla-Consejo Superior de Investigaciones Científicas Avda. Américo Vespucio 49, Isla de la Cartuja, 41092 Sevilla (Spain) E-mail: guzman@us.es

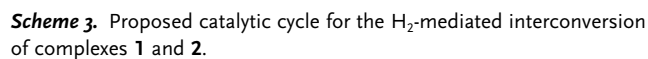
[\*\*] Financial support (FEDER contribution) from the Spanish Ministry of Science (Projects CTQ2010-17476 and Consolider-Ingenio 2010 CSD2007-00006) and the Junta de Andalucía (Grant FQM-119 and Project P09-FQM-4832) is gratefully acknowledged. The use of computational facilities of the Consejo Superior de Investigaciones Científicas (CSIC, Cluster Trueno) and the Centre of Supercomputing of Galicia (CESGA) is also acknowledged. N.R. and J.L.S. thank the MICINN for Ramón y Cajal contracts.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201201811>.



Stirring compound **1** in the absence of H<sub>2</sub> at 20 °C (or at 50–60 °C) for several days did not lead to any reaction, meaning that the prototropic rearrangement (Figure 1 A) that permits interconversion of the two compounds is promoted by dihydrogen. Further studies on this system revealed that in the presence of H<sub>2</sub> complexes **1** and **2** are in dynamic equilibrium. The dihydrogen-induced isomerization occurs between two non-hydride species, and in this regard, it may be recalled that many transition-metal polyhydrides isomerize by consecutive elimination and addition of dihydrogen.<sup>[23]</sup> Recently, Sola and co-workers have reported that dihydrogen catalyzes the *syn/anti* isomerization of five-coordinate iridium monohydride complexes of a pincer PSiP ligand, without involving Ir–H/H<sub>2</sub> atom exchange.<sup>[24]</sup> We found that starting from **1**, a H<sub>2</sub> concentration of about 6 mol % with respect to **1** (as determined by solution <sup>1</sup>H NMR in CD<sub>2</sub>Cl<sub>2</sub>) led at 20 °C to an equilibrium mixture of **2**:**1** of about 4 ( $K_{eq}=4\pm0.5$ ), in a reaction characterized by a half-life  $t_{1/2}$  of about 2.5 h (see the Supporting Information). The same equilibrium mixture was reached starting from pure complex **2**, although longer reaction times were required. The rate of the **1**→**2** isomerization is dependent on the H<sub>2</sub> concentration and, for example, the  $t_{1/2}$  for this transformation under one atmosphere of H<sub>2</sub> (20 °C, CD<sub>2</sub>Cl<sub>2</sub>, 32 mol % with respect to **1**) is about 30 minutes. A series of experiments showed that the possible action of adventitious water and of small amounts of acids or bases could be discounted. A heterogeneous process catalyzed by iridium colloidal particles was equally disproved (see the Supporting Information). Unfortunately, once the equilibrium is attained, and sometimes

On the basis of these results, it seems probable that iridium dihydrogen complexes resulting from coordination of



H<sub>2</sub> to the electrophilic iridium centers of **1** and **2** are key intermediates in their H<sub>2</sub>-catalyzed interconversion (and by extension in that of **3** and **4**). These species (**1**-H<sub>2</sub> and **2**-H<sub>2</sub> in Scheme 3) are structurally analogous to the already discussed carbonyl adducts, **1**-CO and **2**-CO, respectively. Accordingly, their formation requires only relatively facile changes in the coordination mode of the aminopyridinate ligands in the starting complexes **1** and **2**. In the former case, H<sub>2</sub> coordination occurs at the expense of the  $\pi$  component of the Ir-N<sub>amido</sub> bond, whereas in the latter the benzylic terminus shifts from  $\eta^3$  to  $\eta^1$ . As for the isomerization of compound **1** into **2**, whether protonation of the Ir-N<sub>amido</sub> bond of **1** occurs by direct H-H heterolysis of the Ir( $\eta^2$ -H<sub>2</sub>) intermediate, or from an acidic, cationic bis(hydride) complex of Ir<sup>V</sup> resulting from oxidative cleavage of the coordinated H-H bond, cannot be ascertained. Density functional theory calculations (see the Supporting Information) indicate that dihydrogen coordination to iridium in model aminopyridinate complexes is endoergic (by ca. 15 kcal mol<sup>-1</sup>). The resulting dihydrogen and bis(hydride) complexes have comparable relative stabilities and compete in the protonation of the Ir-N<sub>amido</sub> bond. Thus at this level of theory, the calculations do not permit discrimination between the abovementioned mechanistic possibilities for the protonation of the Ir-N<sub>amido</sub> bond. Subsequent activation of a benzylic C-H bond of the pyridine 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> substituent, followed by dihydrogen elimination complete the isomerization with a small energy return of about 1.5 kcal mol<sup>-1</sup>, which is consistent with the experimental observations.

Dihydrogen has always been viewed as an essential reactant for industrial and laboratory syntheses, and for nearly thirty years as an important ligand in coordination and organometallic chemistry. Our reaction system demonstrates that hydrogen is also capable of efficiently and reversibly catalyzing the formation and rupture of the bonds that forms with other common elements. Future research could disclose related catalytic processes involving not only C-H and N-H bonds, but also others, such as O-H or S-H bonds.

Received: March 6, 2012

Revised: May 2, 2012

Published online: June 18, 2012

**Keywords:** C-H activation · dihydrogen catalysis · iridium · ligand isomerization · N-H activation

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