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Dihydrogen Catalysis

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

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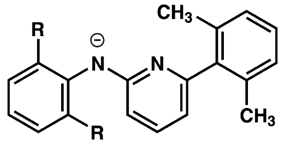
The molecule dihydrogen plays a key role in nature.[1] Although in recent times it has become the ideal energy carrier,[2] its generation in vast quantities by environmentally clean methods is still a major scientific and technical challenge.[3] Nonetheless, H_2 is an essential reagent for many highly important heterogeneous and catalytic processes.[4]

Homogeneous hydrogenations were originally thought to entail oxidative addition and reductive elimination at a metal center,[4b] but the pioneer discovery by Kubas and co-workers of the first sigma-complex of H_2[5] led to a new paradigm that emphasizes the key role of such species in this and other transformations.[6,7] Direct hydrogen transfer from metal–H_2 complexes may occur, an important step in catalytic hydrogenations by electrophilic compounds being heterolytic H_2 activation.[8] H−H heterolysis is relevant to the function of hydrogenases[9–13] and may proceed intramolecularly, with formal proton transfer to a *cis* sulfur, nitrogen, or oxygen donor ligand.[2,9,14–16] In the last years, activation of dihydrogen by compounds of main-group elements has also been demonstrated.[17,18]

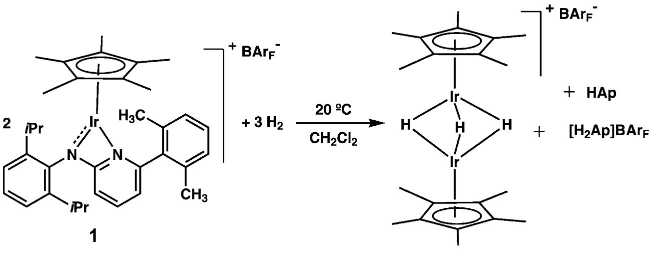
In view of the myriad of stoichiometric and catalytic hydrogenations known, it is plausible that in addition to being a key reagent, the molecule of H_2 could act as a catalyst of important transformations such as the formation and cleavage of H−X bonds in coordination compounds (where X represents for example C, O, N, or S). However, while commonly used ligands, such as N-heterocyclic carbenes, have been shown to catalyze sophisticated organometallic rearrangements,[19] information on catalysis by H_2 is scarce,[20] and to our knowledge it has never been disclosed in a homogeneous system. Herein we show that H_2 catalyzes with high efficiency the formation and rupture of C−H and N−H bonds of iridium-bound aminopyridinate ligands (Scheme 1) in an organometallic system.



Scheme 1. The anionic aminopyridinate ligands employed in this work ($R = iPr$, complexes **1** and **2**; $R = CH_3$, compounds **3** and **4**).

Similarly to somewhat related complexes,[12,21] the aminopyridinate iridium compound **1** (Scheme 2) that contains an $\{(\eta^5\text{-}C_5Me_5)Ir^{III}\}$ unit and an aminopyridinate group in which the amido functionality acts as a σ- and π-donor ligand, reacted with H_2 (CH_2Cl_2, 1 atm) to yield a known dinuclear trihydride,[22] along with an equimolecular mixture of the free and protonated aminopyridine, HAp and $[H_2Ap]BAr_F$, respectively ($BAr_F^- = B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$). 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 1B). In solution they exhibit characteristic ^1H and $^{13}C\{^1H\}$ 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 $2,6\text{-}Me_2C_6H_3$) appear in the ^1H NMR spectrum as a singlet with δ 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 ($^2J_{HH} = 4.5$ Hz). The latter two signals are due to the Ir−CH_2 protons. Furthermore, a new signal attributable to the NH



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

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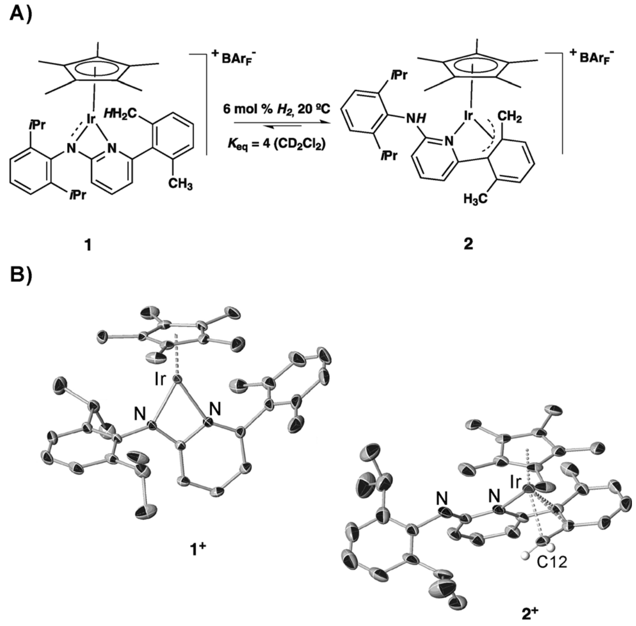


Figure 1. A) H_2 catalyzes the reversible isomerization of complexes **1** and **2**. B) The solid-state molecular structures of complexes **1** and **2**. Ellipsoids set at 30% probability; H atoms (except on C12 in 2^+) and anions are omitted for clarity.

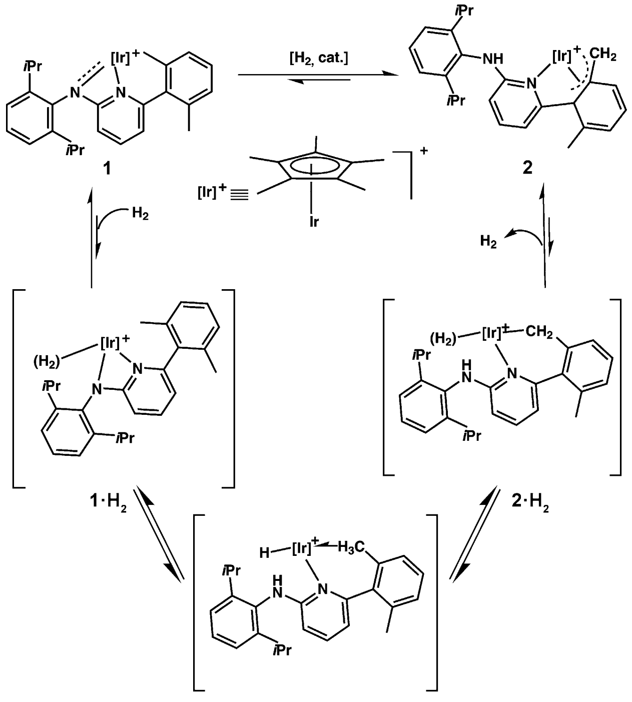
proton of **2** can be found with δ 5.94 ppm. In the ^{13}C NMR spectrum the iridium-bound methylene carbon appears at 34.9 ppm, with a one-bond ^{13}C–^1H NMR coupling constant $^1J_{CH} = 155$ Hz.

Stirring compound **1** in the absence of H_2 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_2 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.[23] 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_2 atom exchange.[24] We found that starting from **1**, a H_2 concentration of about 6 mol% with respect to **1** (as determined by solution ^1H NMR in CD_2Cl_2) led at 20 °C to an equilibrium mixture of **2**:**1** of about 4 ($K_{eq} = 4 \pm 0.5$), 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_2 concentration and, for example, the $t_{1/2}$ for this transformation under one atmosphere of H_2 (20 °C, CD_2Cl_2, 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 before that happens, complexes **1** and **2** abruptly react with H_2 to give the dinuclear trihydride of Scheme 2, in a reaction with an ill-defined and as yet unclear kinetic law.

Interconversion of compounds **1** and **2** entails reversible formation and cleavage of an amido N–H bond and of a benzylic C–H bond of the pyridine 2,6-$Me_2C_6H_3$ substituent. Others have previously observed reversible C–H bond activation reactivity in transition metal-coordinated phosphine, N-heterocyclic carbene, and other ligands.[25–27] To gain mechanistic insight, further experimental and theoretical work was performed. First, a kinetic isotope effect k_H/k_D of 1.3 was measured. This value is nearly identical to that computed (see the Supporting Information) according to the mechanistic route shown in Scheme 3. KIE values close to unity are often observed in reactions of H_2 with unsaturated metal complexes.[24,28] In the reaction of **1** with D_2, deuterium incorporation at the nitrogen and all benzylic sites of the two compounds was observed, although not unexpectedly, deuteration of **1** occurred with a slower rate than for **2**.

Second, the carbonyl adducts **1·CO** and **2·CO** were isolated (Supporting Information, Scheme S1) with ν(C–O) values of 2050 and 2030 cm^{-1}, respectively, that demonstrate the electrophilicity of the iridium centers in parent compounds **1** and **2**.[9] Finally, complexes **3** and **4**, closely related to **1** and **2**, respectively, but having a 2,6-$Me_2C_6H_3$ substituent at the amido (or amine) nitrogen atom (Scheme 1) in place of the bulkier 2,6-$iPr_2C_6H_3$, were also studied. The release of steric pressure at the iridium center caused by this structural modification resulted in a faster dihydrogen catalysis ($t_{1/2}$ ca. 5 min; H_2 concentration ca. 7 mol% with respect to **1**) with no detectable variation in the equilibrium constant ($K_{eq} = 4 \pm 0.5$).

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



Scheme 3. Proposed catalytic cycle for the H_2-mediated interconversion of complexes **1** and **2**.

H_2 to the electrophilic iridium centers of **1** and **2** are key intermediates in their H_2-catalyzed interconversion (and by extension in that of **3** and **4**). These species (**1·H$_2$** and **2·H$_2$** 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_2 coordination occurs at the expense of the π component of the $Ir{-}N_{amido}$ bond, whereas in the latter the benzylic terminus shifts from η^3 to η^1. As for the isomerization of compound **1** into **2**, whether protonation of the $Ir{-}N_{amido}$ bond of **1** occurs by direct H−H heterolysis of the $Ir(\eta^2\text{-}H_2)$ intermediate, or from an acidic, cationic bis(hydride) complex of Ir^V 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. $15\ kcal\,mol^{-1}$). The resulting dihydrogen and bis(hydride) complexes have comparable relative stabilities and compete in the protonation of the $Ir{-}N_{amido}$ bond. Thus at this level of theory, the calculations do not permit discrimination between the abovementioned mechanistic possibilities for the protonation of the $Ir{-}N_{amido}$ bond. Subsequent activation of a benzylic C−H bond of the pyridine $2,6\text{-}Me_2C_6H_3$ substituent, followed by dihydrogen elimination complete the isomerization with a small energy return of about $1.5\ kcal\,mol^{-1}$, 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.

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Communications

Dihydrogen Catalysis

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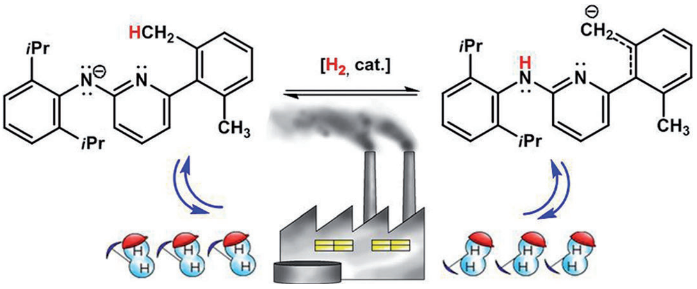

Dihydrogen at work! H_2 catalyzes with high efficiency a prototropic rearrangement of aminopyridinate ligands bound to a {(η^5-C_5Me_5)Ir^{III}} unit. The catalytic isomerization implies reversible formation and cleavage of H–H, C–H, and N–H bonds.