Dihydrogen Complexes

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Computational Evidence for a New Type of η^2-H_2 Complex: When Main-Group Elements Act in Concert To Emulate Transition Metals**

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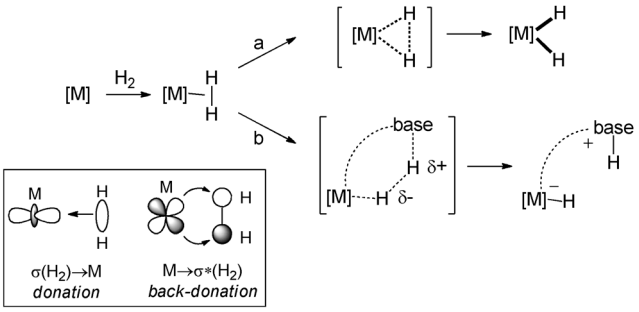
The activation of dihydrogen with transition metals is a process of major and long-standing interest on both synthetic and fundamental grounds.[1] Most catalytic hydrogenation reactions used in industry involve transition metals, and in nature several metalloenzymes are known to efficiently promote H_2 activation/liberation.[2] Basically, two mechanistic pathways can be distinguished for dihydrogen activation at transition metals (Scheme 1). They differ by the presence or absence of an assisting base. In the absence of a base, the transition metal typically cleaves the H–H bond homolytically (oxidative addition) to afford a dihydride complex (route a). Conversely, the presence of a base (external or internal to the coordination sphere) polarizes the H–H bond and induces its heterolytic cleavage. This leads to the formation of a metal hydride with protonation of the base (route b).



Scheme 1. Schematic representation of dihydrogen activation at transition metals, showing the orbital interactions involved in the key η^2-H_2 complex.

In both cases, the first step is assumed to be the formation of an η^2-H_2 complex, also known as an H_2 σ complex[3] (which may correspond to a transition structure or true reactive intermediate). Side-on coordination of H_2 to transition metals arises from the superposition of two bonding interactions: 1) donation of the σ bond of dihydrogen to an empty d orbital of the metal, and 2) back-donation from a d-type occupied orbital of the metal to the σ*(H-H) orbital. The stability of the η^2-H_2 complex depends on the balance between these two interactions.[3] Excessive back-donation weakens the H–H bond and induces ultimately its cleavage.

Recently, the feasibility of dihydrogen activation with non-metals has stimulated intense research,[4] and major breakthroughs have been reported with main-group compounds[5] as well as aminoalkylcarbenes.[6] In particular, phosphine-boranes and related frustrated Lewis pairs (FLPs) have been shown to readily and reversibly activate H_2 under mild conditions (Figure 1), thereby opening new avenues in metal-free catalytic hydrogenation.[7,8] Strikingly, the mechanism of H_2 activation with FLPs differs significantly from that encountered with transition metals.[9] Whereas σ complexes of H_2 have become relatively common species, the side-on coordination of H_2 to boron is extremely rare. Computational studies eventually substantiated the possible existence of such η^2-H_2 complexes.[9b,10–12] However, in the presence of a basic moiety such as a phosphine, end-on interaction of H_2 with the FLP is typically favored. The reluctance of H_2 to coordinate side-on to boranes (relative to transition-metal complexes) stems from the lack of a filled orbital on the Lewis acid that is appropriate for back-donation.[3] In principle, an external donor could provide the necessary electron pair for the stabilization of the η^2-H_2 complex. However, this requires dissymmetric approach to H_2 (for efficient interaction with the σ*(H-H) orbital) resulting in polarization and spontaneous heterolytic cleavage of H_2.

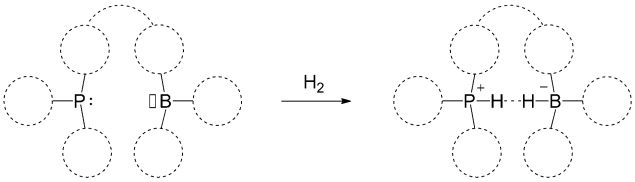


Figure 1. Schematic representation of dihydrogen activation reaction with phosphinoborane FLPs.

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Herein we present theoretical evidence for a new FLP-promoted H_2 activation process involving a new type of η^2-H_2 complex. It arises from the diphosphinoborane **1** (R: *i*Pr, R′: Ph) of Bourissou and co-workers.[13] In terms of FLPs, the two donor groups are positioned close to the Lewis acid moiety and may participate in the reaction with H_2. Related C_2-bridged monophosphinoboranes have been shown to activate H_2,[7d,e,14] and by using the diphosphineborane **1** we aimed to investigate if the second phosphine moiety could exert some particular effect.

The reaction of **1** with dihydrogen (Figure 2) has been studied at various ab initio computational levels.[15] The long-range and dispersion-corrected ωB97Xd functional with the

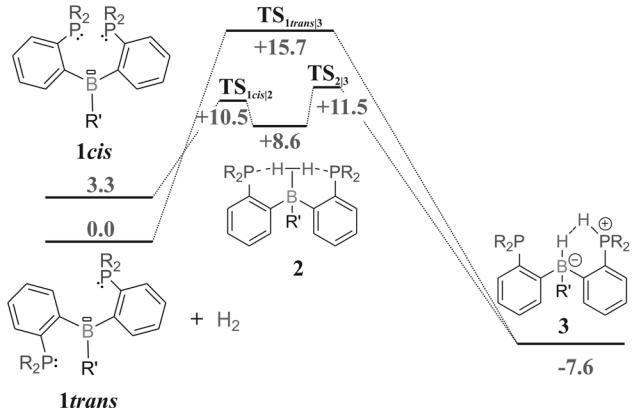


Figure 2. Reaction profile for the activation of dihydrogen by the diphosphineborane **1** (R: *i*Pr, R′: Ph; energies in kcal mol^{-1}).

6-31g(d,2p) basis set and the MP2/def2-TZVPP method resulted in similar geometries and relative energies for the stationary points on the reaction profile as the more economic MPW1K/6-31g(d,2p) level, thus showing the eligibility of the latter for the description of the potential surface of this reaction. Solvent effects (THF) were taken into account by using the PCM solvation method. All the following geometries and relative energies discussed hereafter were obtained at this level of theory.

Several conformers can be considered for the starting material **1**. In particular, the two phosphine side arms may be positioned *trans* to each other (conformer **1*trans***) or both point towards the boron center (conformer **1*cis***). The *trans* conformer, which corresponds to the structure determined crystallographically,[13] is slightly more stable than the *cis* conformer (by 3.3 kcal mol^{-1}), and the rotational barrier associated with the interconversion of **1*trans*** and **1*cis*** is fairly low (9 kcal mol^{-1}). Interestingly, **1*trans*** is predicted to react with H_2 in a similar way as monophosphinoboranes: single-step transformation involving a four-center P···H···H···B interaction (**TS**$_{1trans|3}$, $\Delta E^{\#} = 15.7$ kcal mol^{-1}; Figure 2). Most remarkably, a significantly different pathway is predicted for the *cis* conformer, and the corresponding energy barrier is substantially lower (11.5 kcal mol^{-1}). In this case, the splitting of dihydrogen is preceded by the formation of an intermediate compound (**2**) which is separated from the reactants **1*cis*** + H_2 and product **3** by very low energy barriers (1.9 and 2.9 kcal mol^{-1}, respectively). The phosphonium borate **3** (Figure 3, right) results from the heterolytic cleavage of H_2 and features a classical weak interaction between the protic

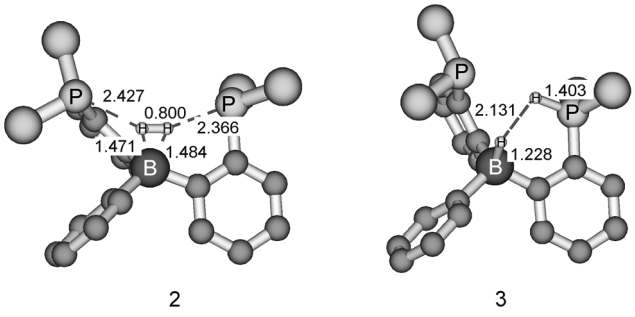
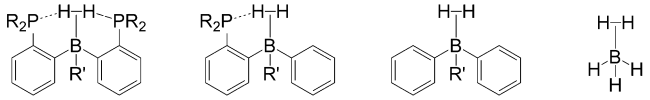


Figure 3. Optimized geometries of the intermediate η^2-H_2 complex **2** and phosphonium borate product **3** (distances in Å).

and hydridic hydrogen atoms (P^+–H···H–B^- dihydrogen bond).[16] Intermediate **2** shows a very different structure (Figure 3, left). The dihydrogen molecule approaches relatively close to the boron center in a side-on fashion. The two hydrogen atoms are placed almost equidistantly from the boron center (d(H-B) = 1.471 and 1.484 Å) and the H–H bond is substantially elongated (d(H-H) = 0.800 Å versus 0.739 Å for H_2 itself). These features are similar to those of the rare examples of η^2-dihydrogen complexes,[9b,10–12] and suggest side-on coordination of H_2 to the boron atom. An additional peculiar feature of intermediate **2** is that the two phosphine groups of **1*cis*** point towards the dihydrogen molecule and engage in weak contacts. The corresponding P···H distances (d(P-H) = 2.366 and 2.427 Å) are well within the sum of van der Waals radii (ca. 2.9 Å).[17] Thus, the interaction of H_2 with **1*cis*** apparently combines side-on coordination to the boron center (with H_2 acting as a donor) and end-on interactions with the two phosphorus atoms (with H_2 acting as an acceptor). Formally, the bonding situation in **2** is reminiscent of that involved in transition-metal complexes of **1**,[18] but with the central transition metal replaced by H_2. The existence and bonding mode of η^2-H_2 complexes such as **2** is without precedent. In all previous studies, the presence of a donor phosphine group in proximity to the Lewis acidic boron center prompted polarization and heterolytic cleavage of the H–H bond.

Atoms in molecules (AIM) and natural bond orbital (NBO) analyses were then carried out to further assess the bonding situation in compound **2** (Table 1). In particular, we aimed at confirming the presence of bonding P···H interactions, estimating their strength, and evaluating their role in the stabilization of the η^2-H_2 complex. As for the reference η^2-H_2/BH_3 complex, the electron density (ρ) at the H–H bond critical point (bcp) substantially decreases upon coordination to boron (from 0.274 au in free H_2 to 0.239 au in **2**). Bond critical points are found between the boron center and the two hydrogen atoms, and the associated ρ(B-H) values are slightly lower in **2** than in the η^2-H_2/BH_3 complex. The electron density map of **2** also shows bonding between the two

Table 1: Results of the AIM and NBO analyses (electron densities at the bcp in atomic units (au), NBO energies in kcal mol^{-1}).



2 **2a** **2b**

		AIM			
		2	**2a**	**2b**	η^2-H_2/BH_3
	ρ(H-H)	0.239	0.240	0.242	0.238
	ρ(B-H)	0.083[a]	0.080[a]	0.076[a]	0.092[a]
	ρ(P-H)	0.023[a]	0.027	–	–
		NBO			
		2	**2a**	**2b**	η^2-H_2/BH_3
ΔE_{int}	σ(H-H)→2p(B)	329.2	314.3	296.0	400.9
	n(P)→σ*(H-H)	9.2[a]	10.3	–	19.4[b]
ΔE_{del}	B/H_2	212.3	197.2	172.2	269.3
	P/H_2	25.6	20.7	–	–

[a] Average value for the two weak interactions. [b] Associated with a donor–acceptor interaction from a σ(B-H) orbital of the BH_3 subunit to the σ*(H-H) orbital.

phosphorus centers and the proximal hydrogen atoms, with electron densities of about 0.023 au.[19]

NBO analysis confirms this bonding picture. At the second-order perturbation level, a donor–acceptor interaction is found between the σ(H-H) orbital and the empty 2p(B) orbital (interaction energy $\Delta E_{int} = 329.2$ kcal mol^{-1} in **2** versus 400.9 kcal mol^{-1} in η^2-H_2/BH_3). Deleting all the interactions between H_2 and boron (to estimate the total interaction energy between these subunits) increases the energy of the complex by 212.3 kcal mol^{-1} (versus 269.3 kcal mol^{-1} in η^2-H_2/BH_3). In addition, two weak interactions arise from donation of the lone pairs of electrons on the phosphorus atom n(P) to the σ*(H-H) orbital ($\Delta E_{int} = 9.5$ and 9.0 kcal mol^{-1}). Deletion of the interactions between H_2 and the two P atoms increases the energy of the complex by 25.6 kcal mol^{-1}. Interestingly, the atomic charges of the two hydrogen atoms remain close to zero in **2** (−0.008 and −0.026). The B···H and P···H interactions result overall in negligible electron transfer between ***1cis*** and H_2, and the lack of H_2 polarization is consistent with the quasisymmetric interaction between H_2 and the diphosphinoborane. The overall bonding situation in **2** is conceptually similar to that encountered in transition-metal/dihydrogen complexes, with donation of H_2 to the boron/metal center and back-donation from the phosphorus atoms/metal center.

To probe the additivity of the interactions between H_2 and the two phosphorus atoms of ***1cis*** calculations were then carried out on model compounds in which one or the two phosphine groups were removed (compounds **2a** and **2b**, respectively). No energy minimum associated with η^2-H_2 structures could be located for these compounds. To draw comparison with the diphosphinoborane system, we thus imposed in **2a** and **2b** the same position of the H_2 molecule relative to the boron center while optimizing the rest of the molecules. The AIM and NBO data indicate that the more phosphorus atoms are appended to the boron atom, the stronger is the side-on coordination of H_2: ρ(B-H) and ΔE_{int} associated with the σ(H-H)→2p(B) interaction increases, while ρ(H-H) decreases from **2b** to **2a**, and **2** (Table 1). The P···H interactions are slightly weaker in **2** ($\Delta E_{int} \approx 9.2$ kcal mol^{-1} each) than in **2a** ($\Delta E_{int} = 10.5$ kcal mol^{-1}), but the two phosphine groups of **2** exert cumulatively a substantially stronger effect than the single phosphine fragment of **2a**. In some way, the dihydrogen molecule seems to act as a relay of electron density between the phosphorus and boron atoms. The absence of an energy minimum associated with a η^2-H_2 complex in the case of **2a** is not the consequence of the lack of back-donation from phosphorus, but rather of its dissymmetric nature. The end-on interaction with a single phosphine group polarizes the H_2 molecule (NBO charges on the two hydrogen atoms are 0.023 and −0.042 in **2a**) and destabilizes the symmetric η^2-H_2 structure.

To further substantiate the role of the stabilizing P···H interactions on the existence of the η^2-H_2 complex, potential surface scans were performed for the reaction of ***1cis*** and ***1trans*** (where the second phosphine group is inert due to its distance from the reaction center) with dihydrogen. The H–H distance was progressively increased starting from the equilibrium geometry of H_2. The energies of the scan points relative to the reactants are displayed in Figure 4. From

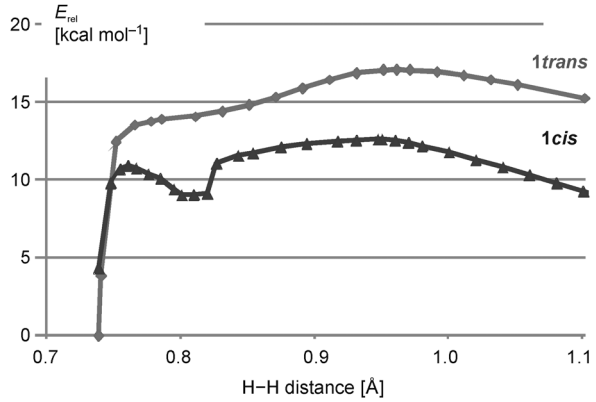


Figure 4. Potential surface scans for the splitting of dihydrogen with ***1cis*** and ***1trans***.

a comparison of the two curves it can be seen that the presence of a second phosphine group, besides decreasing significantly the overall energy barrier, creates a much flatter potential energy surface.

In conclusion, the reaction of the diphosphinoborane **1** with dihydrogen was found to involve an unusual intermediate **2**, in which H_2 coordinates side-on to the central boron center and forms weak contacts with the peripheral donor phosphine groups. These results are indicative of a new mode of interaction between FLPs and H_2, and thereby draw some parallels between main-group elements and transition metals.

The original η^2-H_2 complex **2** is higher in energy than the reactants **1** + H_2 and the heterolytic splitting product **3**, and the related activation barriers are fairly low. It is thus difficult to access **2** for experimental characterization. However, the

basicity of the phosphine groups and acidity of the boron center may provide further stabilization of the η^2-H_2 complex, and future work will seek to analyze substituent effects in detail.

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[19] For comparison, tBu$_2$PhP engages into hydrogen bonding with water, and the associated electron density ρ(P-H) at the bcp was estimated to be 0.022 au (at the same level of theory). No adduct could be found between tBu$_2$PhP and dihydrogen.

