Dihydrogen Activation

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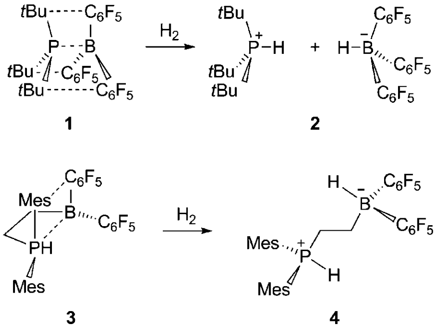
The Mechanism of Dihydrogen Activation by Frustrated Lewis Pairs Revisited**

Stefan Grimme, Holger Kruse, Lars Goerigk, and Gerhard Erker**

Dedicated to Prof. Herbert Dreeskamp on the occasion of his 80th birthday

Activation of dihydrogen is typically a domain of transition metal chemistry.[1] Even nature uses metal-centered reactions to split the dihydrogen molecule in hydrogenase enzymes.[2] A recent development is the use of metal-free systems for H_2 activation: Stephan, Erker et al. have described frustrated Lewis pairs (FLP), that is, pairs of Lewis acids and bases that do not fully quench each other owing to the steric bulk of their substituents; these pairs heterolytically split the H_2 molecule (Scheme 1).[3–6] Phosphane/borane pairs, such as **1** or **3** (and an increasing number of related systems that have appeared in the literature), react rapidly and effectively with H_2 to yield the corresponding phosphonium cation/hydridoborate anion pairs (here **2** and **4**, respectively). These systems have been used as active metal-free hydrogenation catalysts.



Scheme 1. Investigated FLPs that split the H_2 molecule.

Pápai et al.[7] have presented the notion that the H–H bond is cleaved by such systems in an almost linear P-H-H-B arrangement in the transition state (TS). We have now found that this proposal is probably a gross oversimplification of the mechanistic course taken, because the theoretical treatment used did not adequately take into account the interaction between the large substituents that are specifically used. We wish however to point out that the authors in Ref. [7a] pointed out correctly for the first time the importance of secondary, non-covalent $C_6F_5\cdots t\mathrm{Bu}$ interactions. Herein, we present the results of our state-of-the-art calculations for this problem, which has resulted in a more realistic description of the TS involved, which features a non-linear P-H-H-B unit. Furthermore, we present an even simpler mechanistic picture of the basic activation step that emphasizes on the polarization of H_2 induced by the electric field of the FLP inside its cavity that can explain important (and hitherto unclear) experimental findings.

One of the first and very basic questions involves the structure of the TS and in particular in how far the proposed linear P-H-H-B arrangement is required. For the intramolecular system **3** and the similar case of Sumerin et al.,[5c] a linear TS is geometrically not possible, although these systems also efficiently activate H_2 at ambient temperatures.

For molecules **1**–**4**, we performed high-level quantum chemical calculations at wavefunction (WF)-based levels (SCS-MP2[8a] and MP2, extrapolated to the complete basis set [CBS] limit[8b]) and by state-of-the-art dispersion-corrected density functional theory (DFT-D) using the B97-D functional[8c] (for details, see the Supporting Information). For **1**/H_2, we first computed a relaxed two-dimensional potential energy surface (PES) with a fixed linear P-H-H-B unit with the most important H–H and P–B distances as variables. Full TS optimizations were then performed for both **1**/H_2 and **3**/H_2. It should be noted that all our computations refer to isolated molecule conditions; although this makes direct comparisons with experimental observations difficult,[9] we think that it is very important to first pinpoint the mechanism and the associated energies without solvent effects to be on solid ground for further, rather ambitious theoretical condensed-phase treatments.

The two-dimensional PES based on B97-D/TZVPP' optimizations is shown in Figure 1. Furthermore, single-point computations at the MP2/CBS and SCS-MP2/CBS levels, which provide very similar results (Supporting Information), have been performed. The most striking result is that the PESs from all three methods lack the previously observed TS: on the contrary, when the P–B distance decreases, there is

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[*] Prof. Dr. S. Grimme, H. Kruse, L. Goerigk, Prof. Dr. G. Erker
Organisch-Chemisches Institut der Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)
Fax: (+49) 251-83-36515
E-mail: grimmes@uni-muenster.de
erker@uni-muenster.de
Homepage: http://www.uni-muenster.de/Chemie.oc
L. Goerigk
NRW Graduate School of Chemistry
Wilhelm-Klemm-Strasse 10, 48149 Münster (Germany)

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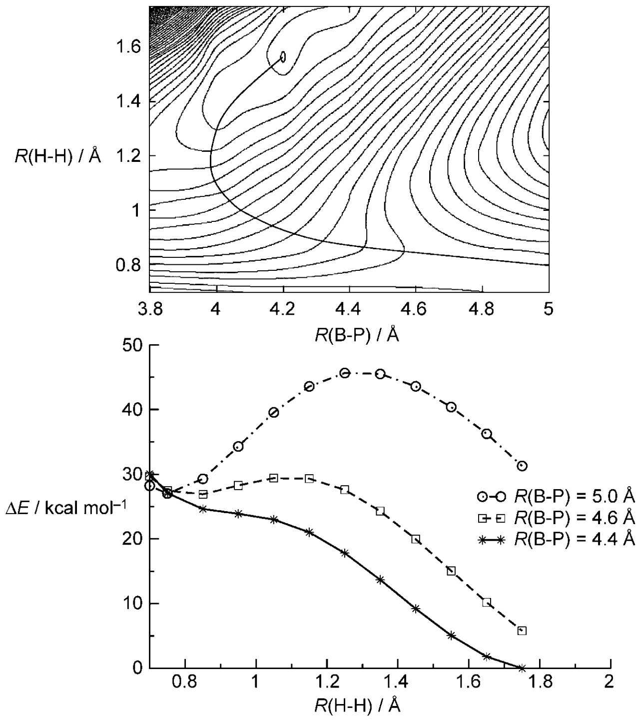


Figure 1. Top: Two-dimensional potential energy surface (the contour line spacing is 2 kcal mol^{-1}) for **1**/H_2 in the linear P-H-H-B arrangement based on B97-D/TZVPP′ optimizations and single-point calculations at the SCS-MP2/CBS(aD-aT) level. The bold line indicates the minimum energy path. Bottom: One-dimensional cuts at three values of *R*(P-B).

a continuous decrease of energy accompanied by a continuous increase of the H–H bond length along the minimum energy path (Figure 1, top) until the product of the reaction (the ion pair) is formed at about *R*(H-H) = 1.6 Å and *R*(B-P) = 4.2 Å for SCS-MP2/CBS. The remaining errors of our quantum chemical treatments are so small (see the results of a CCSD(T) benchmark study for small BR_3/PR_3 systems in the Supporting Information) that this conclusion is rather definite: once the H_2 molecule is within the FLP, the dissociation is practically barrierless. This conclusion is further supported by model calculations (see below). Two rather different theoretical approaches (WF and DFT-D) yield almost identical results, which leads to the conclusion that some kind of entrance process of H_2 into the FLP interior is responsible for a barrier. This conclusion would mean that the reaction of **1** with H_2 is effectively a bimolecular process between a prepared FLP and H_2. The previously reported almost linear TS for **1**/H_2 is likely to be an artifact of the insufficient treatment of intramolecular London dispersion forces between the large substituents. At the applied B3LYP/6-31G* optimization level,[7] such interactions are more or less absent, leading to overly large P–B distances (for example, for the FLP in the equilibrium structure without H_2: about 4.4 Å, compared to 3.96 Å in our treatment). As further explained below, overly large P–B distances artificially create the otherwise non-existing TS (Figure 1, bottom).

The true nature of the TS was further investigated for **1** and **3** by unconstrained optimizations and subsequent computations of the harmonic vibrational frequencies (at the B97-D/TZVPP′ level only). The structures of the first-order saddle points are shown in Figure 2.

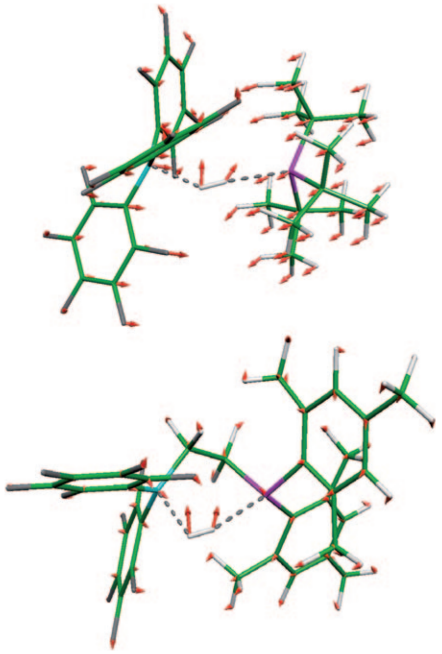


Figure 2. Optimized transition states (B97-D/TZVPP′ level of theory) for dihydrogen activation by **1** (top) and **3** (bottom). The arrows point in the direction of the transition-state normal mode (towards the products).

First, the simpler (truly bimolecular) case of **3**/H_2 will be discussed (Figure 2). All attempts to locate a TS for the attack of the more stable frustrated form of **3** failed (not shown; four-membered ring **3a**, which is more stable than the open gauche form **3b** by 6.1(10.7) kcal mol^{-1}; B97-D/TZVPP’ energy values, SCS-MP2/CBS values in parentheses; for other data, see the Supporting Information). Only for **3b**, which looks similar to the TS structure in Figure 2, were the computations successful, and the results show that an initial preparation step is also involved in the bimolecular system. In the TS, the H–H bond is only slightly elongated from 0.74 to 0.79 Å. The reaction can be classified as being asymmetric/concerted (similar to the activation of norbornene by the same FLP; see Ref. [10]) because the H–B bond is formed slightly earlier than the H–P bond (computed covalent bond orders are 0.22 and 0.15, respectively). The H_2 molecule lies far away from the P–B axis, and overall the structure has the appearance of a typical cyclohexene-type half-chair conformation. The TS mode with a small imaginary frequency of 179 cm^{-1} shows H_2 movement in the expected direction, indicating an early and unstrained TS (geometric preparation energy of only 3.3 kcal mol^{-1}). The computed barrier height with regard to separated H_2 and the quenched form of **3** is reasonably low (14.3(21.5) kcal mol^{-1}) when expected solvent effects are considered, and it is compatible with a reaction at ambient temperatures. The intrinsic barrier (that is, when the energy of opening to **3b** is subtracted) is only 8.2 (10.8) kcal mol^{-1}.

The TS for the trimolecular system **1**/H_2 is remarkably similar in appearance (in particular the movement of the two hydrogen atoms), except that the borane and phosphane fragments move together as the ion pair is formed (Figure 2, top). The P-H-H-B unit, however, is also nonlinear[11] (B-H-H angle 141°, H_2 displacement from B–P axis of about 0.5 Å, H–H distance of 0.80 Å) and the P–B distance is enlarged to 4.6 Å. This result, and the clear bending of one C_6F_5 unit in the TS, shows that the entrance of the H_2 (and the initial opening of the FLP, which is not visible in Figure 2) is the key step of the reaction in this case too. As noted above, once the molecule is inside the FLP cavity (i.e., close to the electric field from the P/B atoms), the reaction proceeds without a barrier, which is in contrast to the conclusion in Ref. [7a]. The barrier computed herein is only 5.2(10.7) kcal mol^{-1}, which is lower than for **3** mainly because of the larger overall exothermicity (−5.0(−1.3) vs. −17.0(−17.9) kcal mol^{-1}). The similar reactivities observed for **1** and **3** can nevertheless be explained if the equilibrium concentration of the FLP for **1** is taken into account.

Can these intriguing results be rationalized further? We believe that this is the case, and propose the simplest (but still correct) theoretical model for the reaction. The FLP as molecular species is neglected entirely and replaced by an electric field (for related theoretical work on H_2 inserted into small polar molecules and the electric field as a catalyst, see Ref. [12]). Almost exact (FCI/aug-cc-pVQZ) potential energy curves for dihydrogen dissociation in an electric field of varying strength applied along the bond axis are shown in Figure 3.

Above a critical field strength of about 0.05–0.06 a.u. (atomic units), the potential energy curves start to exhibit a maximum, which indicates heterolytic dissociation to the H^+H^- ion pair. The corresponding barrier and its position are strongly field-dependent, and for a rather realistic value of about 0.1 a.u., the barrier is lowered to chemically accessible values and eventually even disappears. With increasing field strength the TS moves to smaller H–H distances, and for the lowest curve it reaches a value close to the H–H equilibrium distance that was found in the real TS for the FLPs. The energy near the minimum is much less influenced by the field than the energy in the dissociation regions, which reflects the low polarizability of unstretched H_2. The consequence is that the magnitude of the field along the bond axis in the region of the H_2 molecule should be as large as possible for activation by FLPs. This, however, does not necessarily require a linear arrangement but can be influenced by the polarity and interfragment distance in the FLP. Of course, this simple FLP-free model is incomplete, because in reality the field is not homogeneous, and at some point of the reaction the H_2 acceptors must be present for charge transfer and to pay back the splitting energy (mainly by Coulombic attraction in the ion pair; see Ref. [5c,13]). However, the basic message is that there is no need to involve specific FLP/H_2 orbitals, and that a very classical picture in the Lewis acid/base sense is sufficient to understand the mechanism.

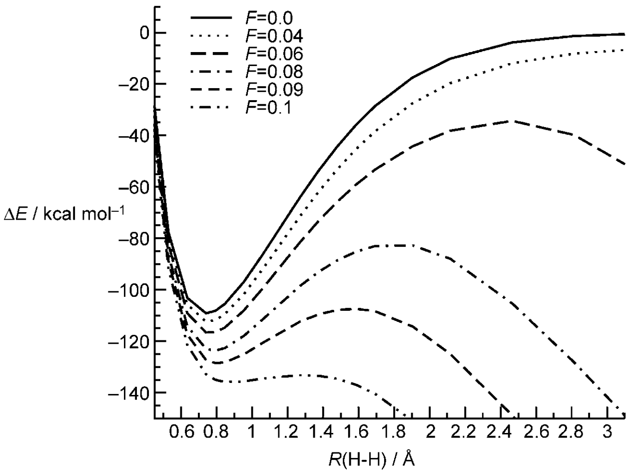
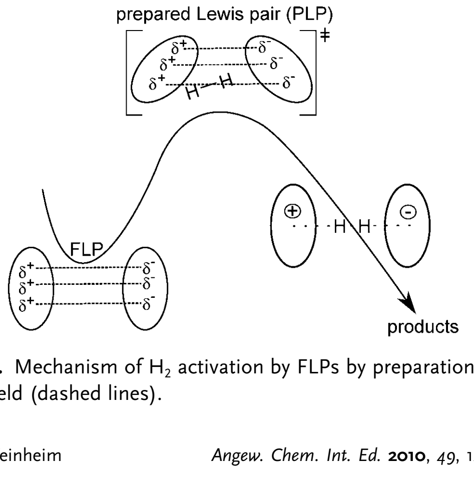


Figure 3. FCI/aug-cc-pVQZ potential energy curves for dihydrogen dissociation in an electric field of varying strength (in atomic units (a.u.); 1 a.u. = 5.1422×10^{11} V m^{-1}). The energy of two hydrogen atoms without field is always set to zero.

In this new view it becomes clear why the chemical behavior of **1** and **3** is so similar although their structures are formally rather different: the electric field strengths in the region of the H_2 molecule in the TS are almost the same (about 0.04–0.06 a.u.). For **1**, such values can be achieved at rather large P–B distances (the field usually increases with decreasing interatomic distance) only when the H_2 molecule is located not too far away from the P–B axis; for **3**, the intrinsically smaller P–B distance (3.25 Å) imposed by the ethano bridge allows stronger deviations from linearity to reach a similar field. This also explains why rather different compounds and in particular bases other than phosphanes, such as amines[5c] or carbenes,[5b] also activate H_2 efficiently.

As first pointed out in Ref. [7a], we think that non-covalent interactions between the bulky substituents are merely necessary to create the interior and to make the FLP flexible enough for the entrance pathway. The more special situation at the boron side of the FLP (a $B(C_6F_5)_n$ moiety with $n > 1$ seems to be required) involves mainly thermodynamic (see reaction energies computed for different substituents in the Supporting Information) and kinetic reasons (stability).

In summary, the new mechanistic insights (Scheme 2) that the FLPs activate by polarization owing to the electric field created by their donor/acceptor atoms and that the observed



Scheme 2. Mechanism of H_2 activation by FLPs by preparation and electric field (dashed lines).

reaction barriers are mainly due to preparation or entrance steps (this can be called a prepared Lewis pair, or PLP) will help to design even more exciting chemistry using the concept of FLPs. This study also shows that sometimes a rather accurate quantum chemical treatment is required to qualitatively obtain the right answer.

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[11] The TS found for **1**/H_2 looks similar to the corresponding TS reported for H_2 activation by a carbene–borane FLP in Ref. [5b]. The computed barrier is only 1.1 $\text{kcal}\,\text{mol}^{-1}$, that is, much less than in Ref. [7a] and more similar to our results. This result, in full agreement with our conclusions, is attributed to the density functional used in Ref. [5b] that better accounts for the interactions between the substituents and thereby indirectly (by shrinking the acid/base distance) lowers the barrier.

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