

## Rationalizing the Reactivity of Frustrated Lewis Pairs: Thermodynamics of H<sub>2</sub> Activation and the Role of Acid–Base Properties

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**Abstract:** The acid–base strengths of recently reported frustrated Lewis pairs and their relation with the thermodynamic feasibility of heterolytic hydrogen splitting reactions are analyzed in terms of quantum chemical calculations. Reaction free energies of hydrogenation processes are computed, and an energy partitioning scheme is introduced, which involves quantitative measures of the acidity and basicity of the reacting Lewis centers. Additional terms are also included that account for possible dative bond formation between the active sites and for stabilizing electrostatic interactions occurring in the product species. For intermolecular combinations of donor–acceptor components, the calculated reaction free energies are found to correlate well with the cumulative acid–base strengths. Product stabilization for these systems represents a notable contribution to the overall energetics; however, it generally shows only a slight variation for the investigated series. The reactivity of linked donor–acceptor pairs is primarily governed by acid–base properties as well, but the magnitude of stabilizing effects arising from acid–base cooperativity of active sites is also of significant importance in determining the thermodynamic feasibility of the reactions.

### 1. Introduction

Bifunctional systems comprising both Lewis acidic and basic functionalities have recently been demonstrated to be versatile ligands, reactants, and efficient catalysts for a wide range of synthetic transformations.<sup>1–3</sup> Experimental findings confirm the role of the acid–base centers of the catalysts in the simultaneous activation of two reactant fragments.<sup>1</sup> However, a cornerstone in the design of successful bifunctional systems is to avoid the unproductive quenching pathways, that is, the direct reaction of the Lewis acid with the Lewis base.<sup>1,2</sup> It has been shown that fine-tuning the hard–soft properties of the Lewis fragments to suppress the dative bond formation is a fruitful approach to

this problem.<sup>4</sup> On the other hand, the possibility of controlling steric factors to ensure Lewis acid–base cooperativity has also been emphasized in the literature.<sup>5</sup>

In the past few years, consequences of steric encumbrance on the reactivity of Lewis pairs were extensively studied by Stephan and co-workers.<sup>6</sup> Preparation of various combinations of bulky Lewis acidic boranes and Lewis basic phosphines, followed by NMR measurements, affirmed that large substituents can indeed completely block the electron pair donation and give rise to “frustrated Lewis pairs”<sup>7</sup> (FLPs) with extraordinary reactivity.<sup>6</sup> In particular, molecular H<sub>2</sub>, which is known to be unreactive toward either the phosphine or the borane component, undergoes rapid heterolytic cleavage when added to the solution of both compounds, forming phosphonium hydridoborates.<sup>8</sup> Heterolytic C–O  $\sigma$  or C–C  $\pi$  bond splitting was also observed for other small molecules such as tetrahydrofuran<sup>9</sup> or ethylene.<sup>10</sup> Quite remarkably, the intramolecularly linked phosphinoborane Mes<sub>2</sub>P–(*p*-C<sub>6</sub>F<sub>4</sub>)–B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> was shown to bind and release

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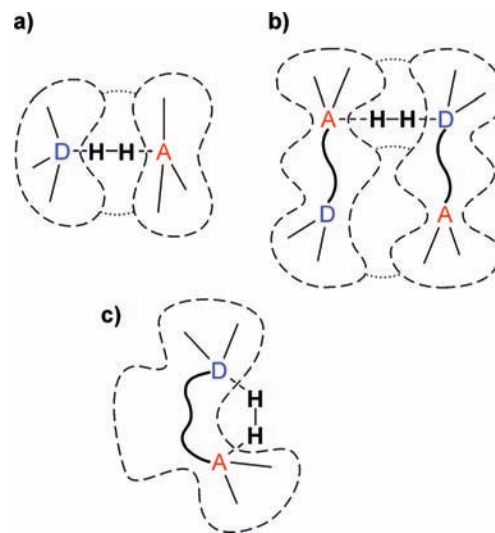
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**Scheme 1.** Heterolytic H<sub>2</sub> Activation via Nonlinked (D/A) and Linked (D~A) FLPs



dihydrogen<sup>11</sup> and also to act as a catalyst in the reduction of C=N and C≡N bonds.<sup>12</sup> These results attracted immediate interest from synthetic chemists because they pave the way for the development of efficient transition-metal-free catalytic hydrogenation processes important from both economical and environmental points of view.<sup>13</sup> Since the first reports on FLP-type chemistry, a number of other combinations of Lewis donor (D) and acceptor (A) molecules, including both nonlinked and linked versions, have been examined and found to cleave H<sub>2</sub> in a heterolytic manner (Scheme 1).<sup>14–30</sup> Some of these D/A and D~A pairs were indeed successfully applied in catalytic hydrogenation processes.<sup>14–20</sup>

Theoretical studies aimed at the understanding of the mechanism of these peculiar reactions<sup>20–23,31–40</sup> actually confirmed the cooperative action of the donor and acceptor sites in



**Figure 1.** Hydrogen splitting in various types of FLPs: *nonlinked* donor–acceptor (D/A) pairs (a), *linked* pairs (D~A) without (b) and with (c) intramolecular preorganization. Dashed lines represent van der Waals surfaces, while dotted lines indicate attractive secondary forces acting between the bulky substituents.

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activating hydrogen<sup>20–22,31–36</sup> or ethylene,<sup>37,38</sup> in close analogy with the heterolytic H<sub>2</sub> splitting with transition metal complexes.<sup>36</sup> However, the computations also revealed the importance of secondary interactions in the preorganization of the reacting partners.<sup>31</sup> The bulky Lewis acid and base, incapable of dative bond formation, may associate to a “frustrated complex” via noncovalent contacts. This reactive intermediate is well prepared for a synergistic interaction with the incoming H<sub>2</sub> molecule (see Figure 1a),<sup>31</sup> which facilitates the splitting process. Involvement of a frustrated complex was also suggested for intramolecular FLPs where the link between the acidic and basic centers does not allow intramolecular cooperation (Figure 1b).<sup>31,32</sup> Nevertheless, with an appropriate arrangement of the reactive sites, linked FLPs may also be able to cleave H<sub>2</sub> in an intramolecular fashion (Figure 1c).<sup>20</sup>

The theoretical studies have also suggested that the absence or weakness of the dative bond corresponds to a strain in the reactive system, which reduces the barrier and makes the reaction more exothermic.<sup>31</sup> However, the rapidly growing body of experimental data on hydrogen splitting reactions indicates that hampering dative bond formation in itself is not sufficient to induce the H<sub>2</sub> cleavage reactivity.<sup>8,28,29</sup> On the basis of the investigation of a series of different phosphines and boranes, Stephan and co-workers concluded that a certain cumulative strength of the Lewis acid and base is necessary for a successful reaction.<sup>8</sup> In addition, Repo, Rieger et al. highlighted the electrostatic interaction between the charged fragments of the zwitterionic products as another important contribution to favorable energetics.<sup>17,20</sup> On the other hand, besides the too low acid–base strength or other factors affecting the thermodynamics of the reaction, kinetic effects alone may also prevent the hydrogen cleavage by FLPs. This has been demonstrated by Erker et al. via the synthesis of phosphinoborane compounds (Mes<sub>2</sub>P–CH=CR–B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, R = CH<sub>3</sub> or Ph) that are unreactive toward H<sub>2</sub> but readily accept the cleaved hydrogen from other systems.<sup>19</sup>

In order to gain deeper insight into the reactivity-determining factors, we now present computational results on the thermodynamics of the hydrogen splitting by various, experimentally

probed, linked, and nonlinked FLPs. The calculated Lewis acid–base properties of the compounds are presented and their influence on the affinity toward hydrogen splitting is discussed. Additional features, namely the effects of possible dative bond formation between the donor and acceptor sites and the stabilizing electrostatic interactions between the charged fragments of the product are also examined and their contribution to the overall reaction free energy is quantified. Fundamental differences between the properties of linked and nonlinked systems are highlighted as well.

## 2. Computational Details

The geometries of all species discussed in this paper were optimized using density functional theory at the M05-2X/6-31G(d) level.<sup>41,42</sup> The M05-2X exchange–correlation functional has been chosen, as it has remarkably good overall performance for the description of main-group element compounds, and it also accounts well for dispersion interactions around the equilibrium distances of weakly bound complexes.<sup>43</sup> The ultrafine integration grid was employed in all calculations, which ensured the stability of the optimization procedure for most of the investigated molecules.<sup>44</sup> For each located stationary point, we carried out vibrational analysis at the same level of theory to confirm that they correspond to true minima. These data were also utilized to compute the zero-point energies and gas-phase thermodynamic corrections in the ideal gas–rigid rotor–harmonic oscillator approximation for  $T = 298.15$  K and  $c = 1$  mol/dm<sup>3</sup>. More accurate electronic energies were computed for the optimized geometries using the larger 6-311++G(d,p) basis set<sup>45</sup> with the M05-2X functional.

The free energies of solvation were estimated in single-point IEF-PCM calculations<sup>46</sup> using the UA0 atomic radii and the M05-2X/6-31G(d) method for the gas-phase optimized geometries. In these calculations, toluene was used as a solvent since the majority of experiments were carried out in this reaction medium. Although the results obtained with the actually used solvents are available as well (see the Supporting Information), our choice for using the same solvent for the entire series of reactions allows us to examine the trends systematically.

Unless stated otherwise in the text, the energy values given in the paper correspond to solvent-corrected Gibbs free energies that are based on M05-2X/6-311++G(d,p) electronic energies and all corrections calculated at the M05-2X/6-31G(d) level. This computational approach is certainly not expected to provide very accurate free energy data mostly due to the empirical ingredients of the polarizable continuum solvent model<sup>47</sup> and the approximations employed in the calculation of gas-phase entropic contributions;<sup>48</sup> however, in the present work, we wish to focus on the trends of calculated reaction free energies as well as on identifying

the influencing factors. For that purpose we think the present approach is fairly adequate.

All calculations presented in the paper were performed using the Gaussian 03 program package.<sup>49</sup>

## 3. Results and Discussion

**Examined Systems.** In order to get a comprehensive picture of the thermodynamics of the H<sub>2</sub> splitting reactions,<sup>50,51</sup> we included a large set of Lewis pairs in our study, for which experiments either clearly indicated hydrogenated product formation ( $[\text{DH}]^+[\text{HA}]^-$  or  $[\text{HD}\sim\text{AH}]^-$ ), or the absence of any reaction with H<sub>2</sub>.

In contributions from various authors, applications of several nonlinked Lewis donors have been reported including a series of phosphines<sup>8,18,24–26</sup> as well as amine,<sup>15–17,28</sup> imine,<sup>14–16</sup> pyridine,<sup>29</sup> and carbene<sup>21,27</sup> bases. In contrast, utilization of only borane acceptors has been described so far in this context, and in most cases it involved tris(pentafluorophenyl)borane, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (denoted as **B** hereafter). The simple, nonlinked combinations of the donor and acceptor compounds we have considered in our study are listed in the first part of Table 1, and the components are shown in Chart 1. Although most D/A pairs were found to interact only weakly or not at all in solution,<sup>52</sup> dative bond formation was observed in a few, sterically less encumbered systems (see Table 1, entries 7, 8, 18, 20). In all cases, a salt of the form  $[\text{DH}]^+[\text{HA}]^-$  is the expected product of the H<sub>2</sub> splitting reaction.

The linked donor–acceptor systems (D~A) we examined are listed in Chart 2 and they include the first successful *p*-C<sub>6</sub>F<sub>4</sub>-connected FLPs (Mes<sub>2</sub>P–C<sub>6</sub>F<sub>4</sub>–**B'** and *t*Bu<sub>2</sub>P–C<sub>6</sub>F<sub>4</sub>–**B'**, where **B'** denotes B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>),<sup>11,12,15</sup> the ethylene- and ethynylene-bridged phosphinoboranes (Mes<sub>2</sub>P–C<sub>2</sub>H<sub>4</sub>–**B'** and *t*Bu<sub>2</sub>P–C<sub>2</sub>HMe–**B'**) reported by the Erker group,<sup>19,23</sup> and the piperidine-borane system **tmp**–CH<sub>2</sub>–C<sub>6</sub>H<sub>4</sub>–**B'** prepared by Repo, Rieger and co-workers.<sup>20</sup> We also carried out calculations for an *o*-phenylene bridged amine-borane (Ph<sub>2</sub>N–C<sub>6</sub>H<sub>4</sub>–**B'**), which was synthesized by Piers et al. prior to the first successes in this field.<sup>53</sup> This latter compound was intended as a potential hydrogen storage device, but the authors did not succeed in the

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(50) Thermodynamics of H<sub>2</sub> uptake/release by small molecules potentially capable of chemical hydrogen storage has been investigated computationally by several authors. See, for example: (a) Staubitz, A.; Besora, M.; Harvey, J. N.; Manners, I. *Inorg. Chem.* **2008**, *47*, 5910. (b) Miranda, C. R.; Ceder, G. *J. Chem. Phys.* **2007**, *126*, 184703. (c) Yang, X.; Hall, M. B. *J. Am. Chem. Soc.* **2008**, *130*, 1798. (d) Grant, D. J.; Arduengo, A. J., III; Dixon, D. A. *J. Phys. Chem. A* **2009**, *113*, 750. (e) Himmel, H.-J.; Schnöckel, H. *Chem.–Eur. J.* **2002**, *8*, 2397.

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(52) Upon mixing the solutions of Mes<sub>3</sub>P + B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and **tmp** + B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, a color change was observed, which points to secondary intermolecular interactions between the molecules. For the latter case, this was also confirmed by NMR chemical shift changes. See refs 8 and 28, respectively.



**Table 1.** Reactions of Lewis Pairs with H<sub>2</sub><sup>a</sup>

entry	reactant(s)	reaction occurs experimentally	reference
Nonlinked FLPs (D/A)			
1	<i>t</i> Bu <sub>3</sub> P + <b>B</b>	yes	8
2	Mes <sub>3</sub> P + <b>B</b>	yes	8
3	(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> P + <b>B</b>	no	8
4	<i>t</i> Bu <sub>3</sub> P + BPh <sub>3</sub>	yes	8
5	Mes <sub>3</sub> P + BPh <sub>3</sub>	no	8
6	<i>t</i> Bu <sub>3</sub> P + BMes <sub>3</sub>	no	8
7	Ph <sub>3</sub> P– <b>B</b>	no	8
8	Me <sub>3</sub> P– <b>B</b>	no	8
9	<b>naph</b> + <b>B</b>	yes, reversibly	18
10	<i>t</i> Bu <sub>3</sub> P + B( <i>p</i> -C <sub>6</sub> F <sub>4</sub> H) <sub>3</sub>	yes	24
11	( <i>o</i> -C <sub>6</sub> H <sub>4</sub> Me) <sub>3</sub> P + B( <i>p</i> -C <sub>6</sub> F <sub>4</sub> H) <sub>3</sub>	yes, reversibly	24
12	Cy <sub>3</sub> P + B( <i>p</i> -C <sub>6</sub> F <sub>4</sub> H) <sub>3</sub>	yes	24
13	( <i>o</i> -C <sub>6</sub> H <sub>4</sub> Me) <sub>3</sub> P + <b>B</b>	yes	24
14	<b>carb</b> + <b>B</b>	yes	21, 27
15	<b>diim</b> + <b>B</b>	yes	15
16	<b>tmp</b> + <b>B</b>	yes	28
17	<b>tmp</b> + BPh <sub>3</sub>	no	28
18	<b>btam</b> – <b>B</b>	yes	15
19	<b>lut</b> + BEt <sub>3</sub>	no	29
20	<b>lut</b> – <b>B</b>	yes	29
Linked FLPs (D~A)			
21	Mes <sub>2</sub> P–C <sub>6</sub> F <sub>4</sub> – <b>B'</b>	yes, reversibly	11
22	<i>t</i> Bu <sub>2</sub> P–C <sub>6</sub> F <sub>4</sub> – <b>B'</b>	yes	7, 12, 15
23	<i>closed</i> -Mes <sub>2</sub> P–C <sub>2</sub> H <sub>4</sub> – <b>B'</b>	yes	23
24	<i>t</i> Bu <sub>2</sub> P–C <sub>2</sub> HMe– <b>B'</b>	yes	19
25	<b>tmp</b> –CH <sub>2</sub> –C <sub>6</sub> H <sub>4</sub> – <b>B'</b>	yes, reversibly	20
26	Ph <sub>2</sub> N–C <sub>6</sub> H <sub>4</sub> – <b>B'</b>	no	53
27	<i>t</i> Bu <sub>2</sub> P– <b>B'</b>	yes	22

<sup>a</sup> Notations: D + A and D–A refer to separated and datively bound nonlinked FLPs, respectively; *closed*-Mes<sub>2</sub>P–C<sub>2</sub>H<sub>4</sub>–**B'** denotes the four-membered ring structure of Mes<sub>2</sub>P–C<sub>2</sub>H<sub>4</sub>–**B'**. Abbreviation **B** is introduced for Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, whereas the B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> unit in linked FLPs is denoted as **B'**.

preparation of the hydrogenated form, which they attributed to the low basicity of the triaryl-substituted nitrogen atom.

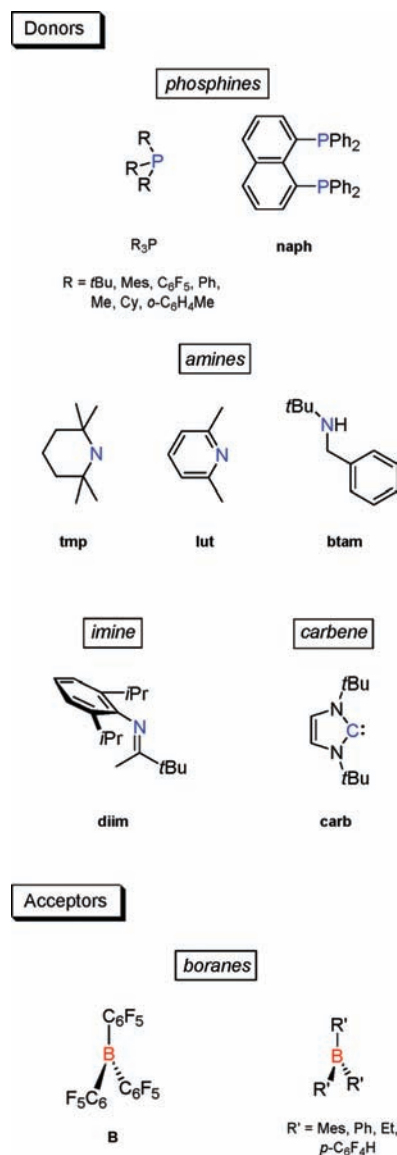
No signs of an intra- or intermolecular dative bond were observed for the above systems, except for the ethylene-linked Mes<sub>2</sub>P–C<sub>2</sub>H<sub>4</sub>–**B'** molecule, which is stable as a four membered heterocycle with a P–B bond.<sup>23</sup> This heterocyclic structure will be referred to as *closed*-Mes<sub>2</sub>P–C<sub>2</sub>H<sub>4</sub>–**B'**, while we denote the structure without the P–B bond simply as Mes<sub>2</sub>P–C<sub>2</sub>H<sub>4</sub>–**B'**, in analogy with the other systems.

In addition to these D~A molecules, a directly linked R<sub>2</sub>P–BR'<sub>2</sub> type compound (*t*Bu<sub>2</sub>P–**B'**) was also included in our study.<sup>22</sup> Similar phosphinoboranes without steric hindrance form datively bound dimers with a PBPB ring; however, the investigated species remains monomeric. Although a π-type overlap between the adjacent phosphorus lone pair and boron empty orbital can be identified, the molecule keeps sufficient Lewis acidic and basic character to react with H<sub>2</sub> directly, and therefore this system can also be classified as an intramolecular frustrated pair with unquenched donor and acceptor abilities.<sup>22,54</sup>

Hydrogenation of all compounds of this family yields (or is expected to yield) the appropriate ammonium or phosphonium hydridoborate zwitterions [<sup>+</sup>HD~AH<sup>−</sup>]. The experimental observations are summarized in the second part of Table 1.

(53) Roesler, R.; Piers, W. E.; Parvez, M. J. *Organomet. Chem.* **2003**, 680, 218.

(54) Privalov and coworkers have analyzed H<sub>2</sub> uptake by a series of directly linked R<sub>2</sub>P–BR'<sub>2</sub> compounds computationally. The authors pointed out the importance of destabilizing the intramolecular P–B dative π bond as well as increasing Lewis acidity to achieve lower activation energies. The exothermicities of the processes were also calculated but not discussed in detail. See ref 40.

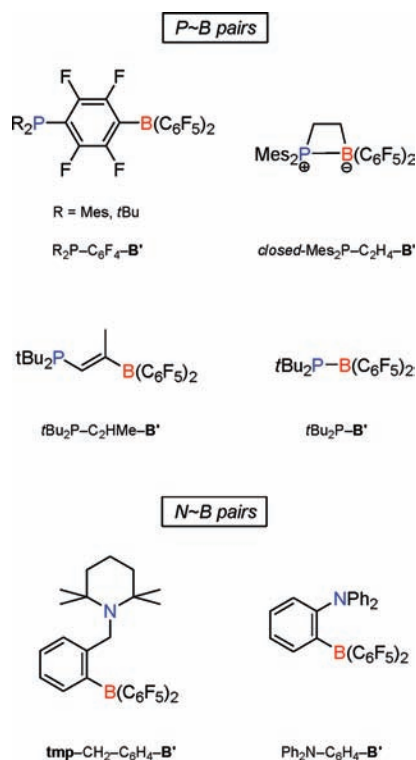
**Chart 1.** Investigated Lewis Donors and Acceptors

**Overall Thermodynamics.** To address the thermodynamic feasibility of the H<sub>2</sub> cleavage reaction, we first calculated the overall solvent-phase Gibbs free energies ( $\Delta G$ ) of the H<sub>2</sub> activation for the investigated D/A and D~A systems (see reactions 1 and 2 in Scheme 1). As indicated in Table 1, we adopted the experimentally found stable forms (datively bound or unbound) of the cooperative Lewis acid–base systems on the reactant side. The product was treated as a solvated cation–anion pair [DH]<sup>+</sup>[HA]<sup>−</sup> or a single zwitterionic species [<sup>+</sup>HD~AH<sup>−</sup>].<sup>55</sup> For the nonlinked pairs, the geometry optimizations of the product molecules were performed from initial structures having the D–H and A–H bonds oriented toward each other, which may give rise to D–H⋯H–A type dihydrogen bonds.<sup>56,57</sup> Although this arrangement is consistent with the suggested mechanism of heterolytic H<sub>2</sub> splitting, it does not

(55) It must be noted that the precipitation of the product from the solution has been observed during the reaction course in most cases. The obviously exergonic crystallization step provides additional stabilization for the product, which is not included in the calculated free energies.

(56) (a) Custelcean, R.; Jackson, J. E. *Chem. Rev.* **2001**, 101, 1963. (b) Bakhmutov, V. I. *Dihydrogen Bonds*; Wiley-VCH, New York, 2008.

Chart 2. Investigated Linked FLPs



necessarily correspond to available X-ray data. For such systems ( $Cy_3P/B(p-C_6F_4H)_3$  and **carb/B**), we have considered product isomers from crystallographic structures as well, but for the sake of comparison, the reported energetics refers to  $D-H\cdots H-A$  structures for all  $[DH]^+[HA]^-$  compounds. In the case of the linked  $D\sim A$  and  $[^+HD\sim AH^-]$  species, the initial structures were chosen on the basis of available crystallographic data.<sup>58</sup>

The computed solvent-phase  $\Delta G$  data of the investigated Lewis pairs are presented on an energy scale shown in Figure 2.<sup>59</sup> It is apparent from these results that the calculated free energies vary in a remarkably wide range (from  $-40$  to  $+30$  kcal/mol). All systems that were shown to be unreactive experimentally are characterized by positive  $\Delta G$  values typically above  $+10$  kcal/mol, which suggests that the absence of the  $H_2$  cleavage can be attributed to the thermodynamically unfavorable nature of these reactions. On the other hand, for all reactive systems but one, we obtained free energy values that are slightly or in some cases well below zero. The exception is the  $tBu_3P + BPh_3$  pair, which was found to be reactive, yet the calculated  $\Delta G = +18.2$  kcal/mol clearly falls into a region of several nonreactive systems. This sharp contradiction between theory and experiment will be commented on later in our paper.

Some of the FLPs listed in Table 1 are known to activate  $H_2$  reversibly (entries 9, 11, 21, 25), i.e., they lose  $H_2$  and reform the original compounds upon exposure to heat or/and reduced pressure.<sup>60</sup> Although these nonequilibrium conditions are not taken into account in our present theoretical approach, one

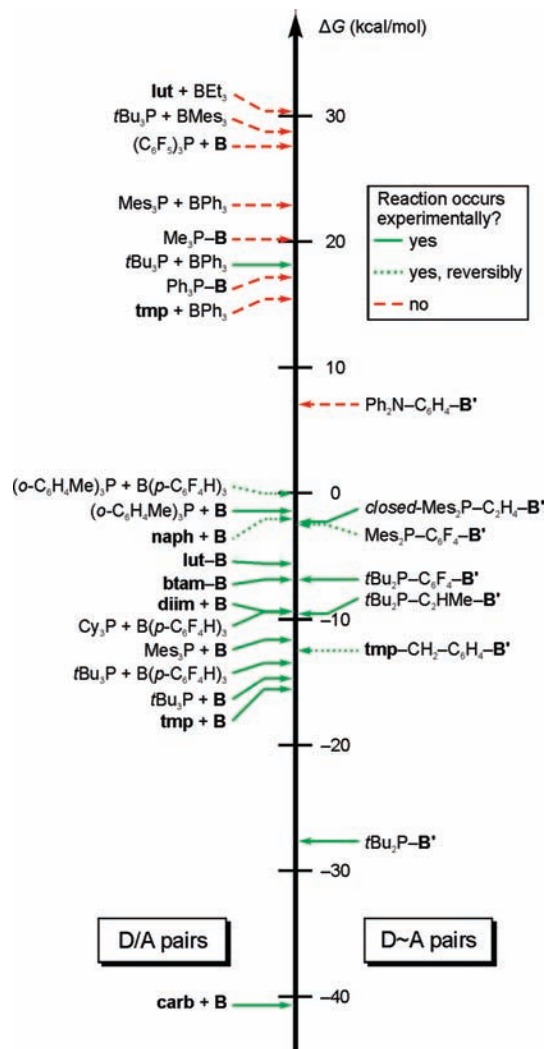


Figure 2. Calculated Gibbs free energies for the hydrogen splitting reaction of Lewis pairs.

expects that reversible FLP/ $H_2$  systems are slightly exergonic in the direction of  $H_2$  uptake at standard conditions. The calculated free energies for the  $(o-C_6H_4Me)_3P + B(p-C_6F_4H)_3$  and **naph** + **B** pairs ( $-0.1$  and  $-2.1$  kcal/mol) are in good accordance with this expectation. The agreement is still acceptable for the  $Mes_2P-C_6F_4-B'$  +  $H_2$  reaction ( $\Delta G = -2.5$  kcal/mol), but the computed Gibbs free energy for  $H_2$  splitting with the **tmp-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-B'** "molecular tweezer"<sup>20</sup> seems too low ( $\Delta G = -12.5$  kcal/mol). This apparent contradiction could probably be attributed to the uncertainties of the applied methodology (see Computational Details), and additional efforts will be required for comprehensive understanding.<sup>61</sup>

**Partitioning of the Overall Free Energy.** To understand the origin of the remarkable difference between the free energies of the various reactions, we partitioned the hydrogen splitting reaction into five hypothetical, but chemically meaningful, steps.<sup>51,62</sup> The primary motivation behind this partitioning was to include quantitative measures of the acidity and basicity of

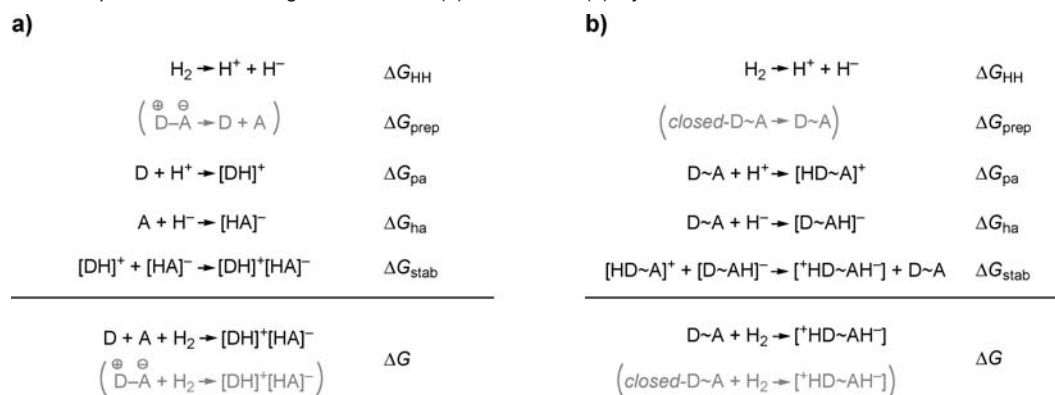
(57) For recent theoretical studies on model systems, see: (a) Hugas, D.; Simon, S.; Duran, M.; Guerra, C. F.; Bickelhaupt, F. M. *Chem.-Eur. J.* **2009**, *15*, 5814. (b) Krapp, A.; Frenking, G.; Uggerud, E. *Chem.-Eur. J.* **2008**, *14*, 4028.

(58) More details about the molecular geometries used to calculate the thermodynamic data are given in the Supporting Information.

(59) All energy data discussed in our paper are listed in tabular format in the Supporting Information.

(60) The **lut-B** system also shows  $H_2$  loss but only upon heating in the presence of pyridine, which shifts the equilibrium due to the formation of the stable pyridine-B adduct; see ref 29.

(61) This reaction is predicted to be highly exergonic at the PBE/6-31G(d) level as well ( $\Delta G = -7.3$  kcal/mol) as reported by Repo, Rieger, and co-workers. See ref 20.

Scheme 2. Reaction Steps of the Partitioning for Nonlinked (a) and Linked (b) Systems<sup>a</sup>

<sup>a</sup> Reaction steps shown in gray refer to FLPs forming dative bonds in equilibrium.

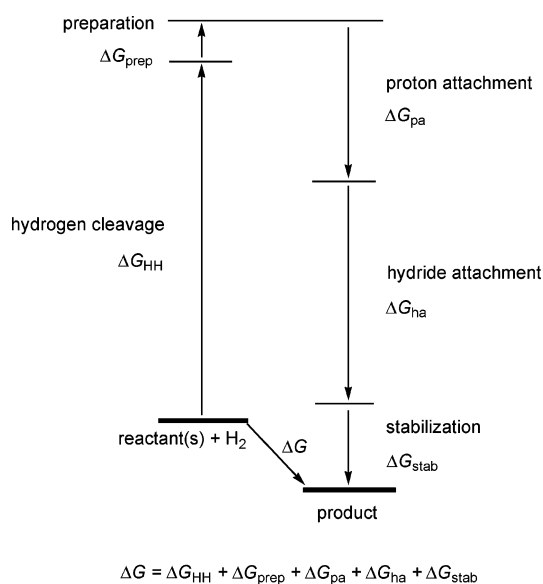


Figure 3. Partitioning of the reaction free energy.

the reacting Lewis centers, which were suggested by the Stephan group to play key role in determining the reactivity.

Several methods have been proposed in the literature for the quantification of Lewis donor and acceptor strengths.<sup>63</sup> The methods are usually based on NMR or IR spectroscopic properties, on the calculated electronic structure of particular adducts, or on thermodynamic data of adduct formation with a given partner. For the present purpose, the Gibbs free energies of proton and hydride attachments to the donors and acceptors seemed the most appropriate choice. These two quantities form the basis of the partitioning, which were supplemented by additional terms that were chosen to be as simple as possible yet to sum up to the overall free energy of the hydrogen splitting. The general partitioning scheme is presented in Figure 3, whereas the thermodynamic cycles associated with the hydrogenation reactions of D/A and D~A Lewis pairs are shown in Scheme 2.

According to the energy decomposition we propose, the first step of the thermodynamic cycle is the *heterolytic cleavage of dihydrogen* into  $\text{H}^+$  and  $\text{H}^-$  ions in toluene.<sup>64</sup> This is a rather endergonic process with a calculated free energy of  $\Delta G_{\text{HH}} = +128.8$  kcal/mol, which is constant for all FLPs.<sup>65</sup> For most of the examined systems, where no dative bond between the Lewis centers exists in equilibrium, this is the only step uphill in free energy. However, if the active sites are quenched, an additional amount of free energy ( $\Delta G_{\text{prep}}$ ) is required to break the intra- or intermolecular dative bonds, so that the donor and acceptor centers become *prepared* to receive the  $\text{H}^+$  and  $\text{H}^-$  ions.

For the nonlinked systems, we adopted the Gibbs free energies of the *attachment of a proton* ( $\Delta G_{\text{pa}}$ ) and a *hydride* ( $\Delta G_{\text{ha}}$ ) ion to the donor or acceptor molecules as the following two terms of the partitioning. As a consequence, the final, *stabilization* step corresponds to the formation of the product ion pair from the separated  $[\text{DH}]^+$  and  $[\text{HA}]^-$  ions (see Scheme 2a). The free energy  $\Delta G_{\text{stab}}$  associated with this step is simply the binding free energy of the ion pair.

For the linked pairs, which are in fact ambiphilic molecules, the acid and base strengths of the corresponding sites are defined as the free energies of proton and hydride attachments to the D~A compounds ( $\Delta G_{\text{pa}}$  and  $\Delta G_{\text{ha}}$  in Scheme 2b). Consequently, the last step of the thermodynamic cycle is the reaction of the ionic  $[\text{HD}\sim\text{A}]^+$  and  $[\text{D}\sim\text{AH}]^-$  species that yields the zwitterionic  $[{}^+\text{HD}\sim\text{AH}^-]$  product and a neutral D~A molecule. The free energy of this step ( $\Delta G_{\text{stab}}$ ) is a measure of stabilizing effects arising from the acid–base cooperativity of active centers, i.e., the enhancement of Lewis acidity upon protonation of the basic site or vice versa.

**Term by Term Analysis.** The partitioning of the overall reaction free energy allows a quantitative assessment of the most important factors that control the thermodynamic feasibility of hydrogenation processes. We shall therefore analyze each term of the decomposition separately.

One of the key elements of the FLP concept is that the steric effects of the bulky substituents preclude or weaken the dative donor–acceptor bonding giving rise to inherent or thermally induced frustration.<sup>33</sup> As pointed out previously, the reactant-state destabilization decreases the activation barrier and con-

(62) A partitioning (different from the present scheme) was also invoked by Harvey, Manners, and co-workers to elucidate factors controlling  $\text{H}_2$  releasing thermodynamics in amine–borane adducts. See ref 50a.  
 (63) For methods of determination of Lewis acidity or basicity, see the following papers as well as references therein: (a) Denmark, S. E.; Beutner, G. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 1560. (b) Piers, W. E. *Adv. Organomet. Chem.* **2004**, *52*, 1. (c) Reference 7.

(64) For the details on the estimation of the solvation free energy of  $\text{H}^+$  in toluene, see the Supporting Information.

(65) The calculated gas-phase  $\Delta H$  for this reaction is +398.4 kcal/mol, which is in good agreement with the experimental value of +400.4 kcal/mol (see ref 66).

(66) Goebbert, D. J.; Wenthold, P. G. *Int. J. Mass Spectrom.* **2006**, *257*, 1.



**Table 2.** Calculated Preparation Gibbs Free Energies of Some Lewis Pairs<sup>a</sup>

Lewis pair	$\Delta G_{\text{prep}}$ (kcal/mol)
Me <sub>3</sub> P– <b>B</b>	23.4
Ph <sub>3</sub> P– <b>B</b>	11.1
<b>btam</b> – <b>B</b>	7.1
<i>closed</i> -Mes <sub>2</sub> P–C <sub>2</sub> H <sub>4</sub> – <b>B'</b>	5.8
<b>lut</b> – <b>B</b>	5.5

<sup>a</sup> For all other pairs:  $\Delta G_{\text{prep}} = 0$ .

tributes to the exothermicity of the reaction.<sup>31,67</sup> In the present partitioning, this aspect of FLP-type H<sub>2</sub> activation is reflected by the fact that most of the Lewis pairs possess zero free energy of preparation, i.e., the active sites are free in equilibrium. Three reactive systems (**btam**–**B**, **lut**–**B**, and *closed*-Mes<sub>2</sub>P–C<sub>2</sub>H<sub>4</sub>–**B'**) were calculated to have small  $\Delta G_{\text{prep}}$  values ranging between 5 and 8 kcal/mol (see Table 2).<sup>68</sup> As expected, the sterically less crowded Me<sub>3</sub>P and Ph<sub>3</sub>P donors form stronger dative bonds with **B**, although the calculated data suggest that the Ph<sub>3</sub>P–**B** adduct exhibits a considerable degree of strain.<sup>69</sup>

The basicity<sup>70</sup> of the donor compounds or donor sites of the linked systems is quantified by the Gibbs free energy of proton attachment ( $\Delta G_{\text{pa}}$ , see Figure 4). We note that commonly used definitions involve thermodynamic data of the reverse process.<sup>71</sup> With the opposite sign convention used here, a more negative  $\Delta G_{\text{pa}}$  value corresponds to a stronger donor ability.<sup>68</sup>

The calculated data reveal that most nonlinked bases with N or P donor atoms fall into a range of only about 15 kcal/mol. Despite the variety in the structures of the substituents, some trends can be clearly identified. As expected, phosphines with bulky alkyl groups are more basic than Ph<sub>3</sub>P. The increasing basicity in the order of Ph<sub>3</sub>P, (*o*-C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>P, and Mes<sub>3</sub>P reflects the electronic effect of methyl substitution, whereas the introduction of electron-withdrawing substituents on the aromatic rings dramatically decrease the basicity in (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>P. The extremely high proton affinity of base **carb** is borne out by its separation from the group of phosphines and amines on the  $\Delta G_{\text{pa}}$  scale.

The relative ordering of the linked systems also lends itself easily to chemical interpretation. The three most basic compounds possess alkylamine, alkylphosphine, or mesitylphosphine fragments and form a group between –45 and –50 kcal/mol. The electron-withdrawing effect of the fluorophenylene linker in Mes<sub>2</sub>P–C<sub>6</sub>F<sub>4</sub>–**B'** and *t*Bu<sub>2</sub>P–C<sub>6</sub>F<sub>4</sub>–**B'**, or the directly attached B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> moiety in *t*Bu<sub>2</sub>P–**B'** notably reduces the basicity of the phosphorus. The triaryl amine fragment of Ph<sub>2</sub>N–C<sub>6</sub>H<sub>4</sub>–**B'**, featuring an almost completely planar nitrogen atom, has significantly diminished basicity.<sup>53</sup>

The calculated acidity of the acceptor centers, measured by the Gibbs free energy of hydride attachment ( $\Delta G_{\text{ha}}$ ), is shown in Figure 5.<sup>68</sup> Thermodynamic quantities pertinent to the reverse process are usually referred to as “hydride affinity” or “hydride

donor ability”, and they are often used to characterize Lewis acids including transition metal complexes.<sup>51,66,72</sup>

According to the data presented in Figure 5, the number of fluorine atoms on the substituents plays an essential role in determining the acceptor strength of the boron atom. The scale starts from the strongest and the most frequently employed Lewis acid **B**.<sup>73</sup> Replacement of para-fluorines with hydrogen atoms (B(*p*-C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub>) or with an R<sub>2</sub>P fragment (Mes<sub>2</sub>P–C<sub>6</sub>F<sub>4</sub>–**B'** and *t*Bu<sub>2</sub>P–C<sub>6</sub>F<sub>4</sub>–**B'**) leads to a slight decrease in acidity. A greater skip on the scale stems from substituting the alkyl or R<sub>2</sub>P groups for a whole C<sub>6</sub>F<sub>5</sub> ring (five D~A compounds between –55 and –60 kcal/mol). The complete removal of the F atoms drops the acidity by ~30–40 kcal/mol and yields remarkably lower acceptor strength for BPh<sub>3</sub> as compared to **B**, which is consistent with previous experimental and theoretical findings.<sup>74</sup> Among the nonfluorinated compounds (BPh<sub>3</sub>, BMes<sub>3</sub>, and BEt<sub>3</sub>), electronic effects of the substituents easily explain the ordering.

The final contribution to the overall free energy of the hydrogen splitting reaction is  $\Delta G_{\text{stab}}$  (see the definition in Scheme 2), which covers the inter- or intramolecular interaction of the charged fragments of the product. In order to assess the effect of the molecular structure on  $\Delta G_{\text{stab}}$  and the significance of electrostatics, we plot the calculated data as a function of the reciprocal of the distance of the donor and acceptor atoms in the product ( $d_{\text{DA}}^{-1}$ ; see Figure 6).

It is apparent from these results that the vast majority of the nonlinked systems can be characterized by a stabilization free energy lying in a fairly narrow range between –14 and –24 kcal/mol. The modest variation of this term can be associated with the structural similarity of the [DH]<sup>+</sup>[HA]<sup>–</sup> ion pairs. In all cases, D and A bear +1 and –1 formal charges, which are shielded by bulky apolar groups, and their distance falls in the range of approximately 3.5–4.5 Å ( $d_{\text{DA}}^{-1} = 0.22$ – $0.29$  Å<sup>–1</sup>). The stabilization in [tmpH]<sup>+</sup>[HBPh<sub>3</sub>]<sup>–</sup> and [lutH]<sup>+</sup>[HBEt<sub>3</sub>]<sup>–</sup> is stronger than the average, which can be related to the weaker steric repulsion owing to the small size of the constituent molecules. The reduced  $\Delta G_{\text{stab}}$  values obtained for the [Ph<sub>3</sub>PH]<sup>+</sup>[HB]<sup>–</sup>, [naphH]<sup>+</sup>[HB]<sup>–</sup>, and [Cy<sub>3</sub>PH]<sup>+</sup>[HB(*p*-C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub>]<sup>–</sup> products are due to better accessibility of the P–H bond by the solvent in the phosphonium cations, i.e., enhanced solvent stabilization of the [R<sub>3</sub>PH]<sup>+</sup> ions, as compared to product ion pairs.<sup>75</sup> According to Figure 6, no clear correlation between  $\Delta G_{\text{stab}}$  of the nonlinked systems and  $d_{\text{DA}}^{-1}$  can be observed, which indicates that the interaction strength is the result of an interplay between more factors (electrostatics, dispersion, repulsion, solvation effects, etc.).<sup>76</sup>

The existence of intermolecular D–H···H–A dihydrogen bonds in the [DH]<sup>+</sup>[HA]<sup>–</sup> ion pairs, which has been noted

(67) For reviews concerning the assistance of the strain in the reactants, see: (a) Brown, H. C. *J. Chem. Soc.* **1956**, 1248. (b) Comba, P. *Coord. Chem. Rev.* **2000**, 200–202, 217.

(68) For a comparison of the calculated values with available experimental data, see the Supporting Information.

(69) Group 13–15 donor–acceptor complex dissociation energies have been studied recently. See: Gille, A. L.; Gilbert, T. M. *J. Chem. Theory Comput.* **2008**, 4, 1681.

(70) Concerning ab initio determination of basicity of various compounds in organic solvents, see: Li, J.-N.; Fu, Y.; Liu, L.; Guo, Q.-X. *Tetrahedron* **2006**, 62, 11801, and references therein.

(71) Proton affinity usually refers to  $\Delta H$ , the pK<sub>a</sub> value is proportional to  $\Delta G$  of the proton detachment reaction.

(72) (a) Vianello, R.; Maksić, Z. B. *Inorg. Chem.* **2005**, 44, 1095. (b) Maksić, Z. B.; Vianello, R. *Pure Appl. Chem.* **2007**, 79, 1003. (c) Campodónico, P. R.; Aizman, A.; Contreras, R. *Chem. Phys. Lett.* **2009**, 471, 168. (d) Zhu, X.-Q.; Liang, H.; Zhu, Y.; Cheng, J.-P. *J. Org. Chem.* **2008**, 73, 8403. (e) Kovács, G.; Pápai, I. *Organometallics* **2006**, 25, 820.

(73) For reviews on the application of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in synthetic chemistry, see: (a) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, 26, 345. (b) Erker, G. *Dalton Trans.* **2005**, 1883. (c) Focante, F.; Mercandelli, P.; Sironi, A.; Resconi, L. *Coord. Chem. Rev.* **2006**, 250, 170. (d) Reference 63b.

(74) See, for example: (a) Timoshkin, A. Y.; Frenking, G. *Organometallics* **2008**, 27, 371. (b) Morrison, D. J.; Piers, W. E. *Org. Lett.* **2003**, 5, 2857. (c) Bradley, D. C.; Harding, I. S.; Keefe, A. D.; Motevalli, M.; Zheng, D. H. *J. Chem. Soc., Dalton Trans.* **1996**, 3931. (d) Britovsek, G. J. P.; Ugolotti, J.; White, A. J. P. *Organometallics* **2005**, 24, 1685.

(75) For details, see Supporting Information.

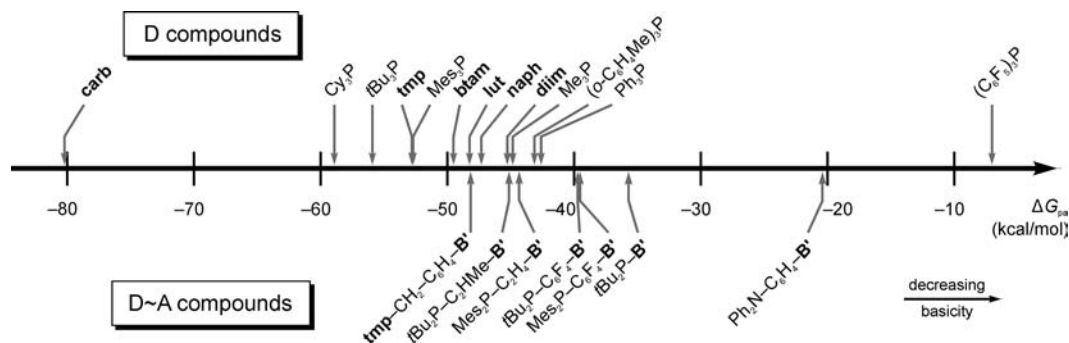


Figure 4. Calculated Gibbs free energies of the proton attachment to the Lewis donors.

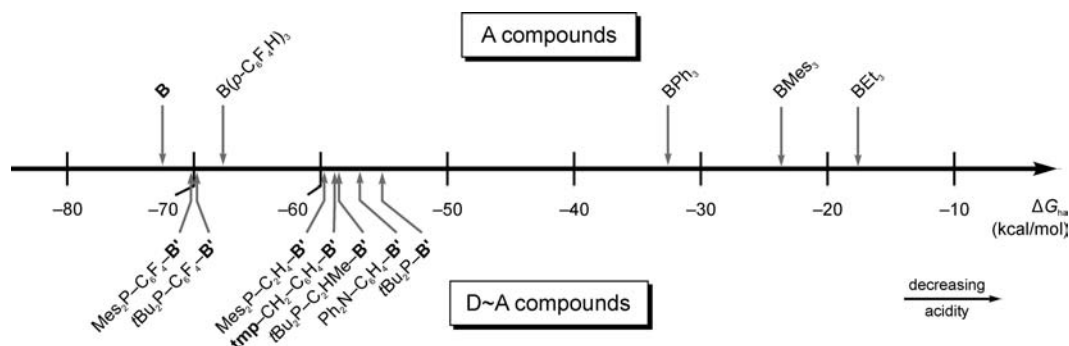


Figure 5. Calculated Gibbs free energies of the hydride attachment to the Lewis acceptors.

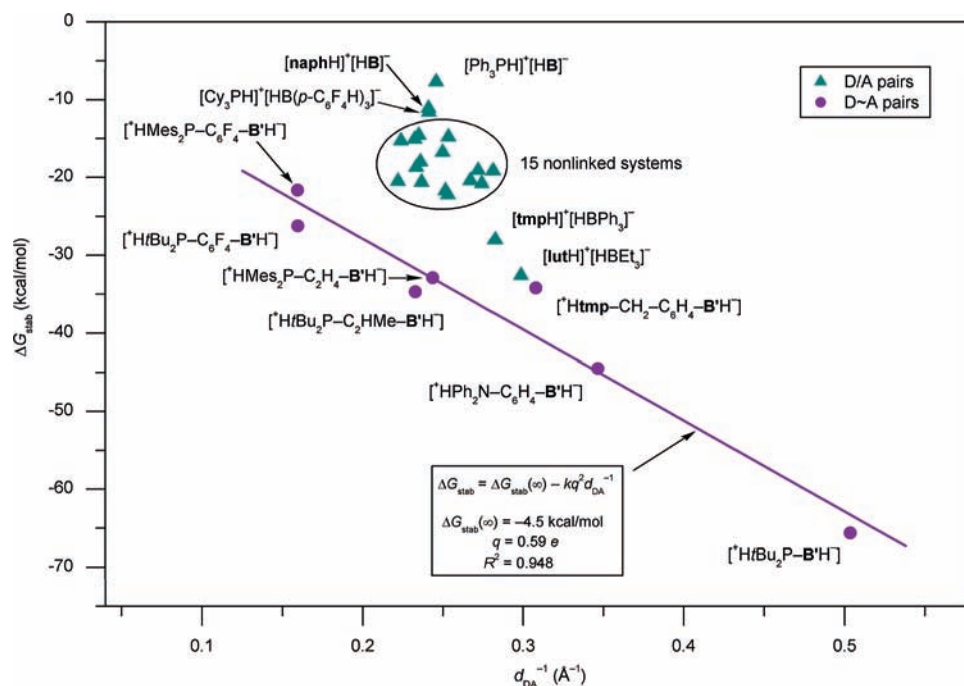


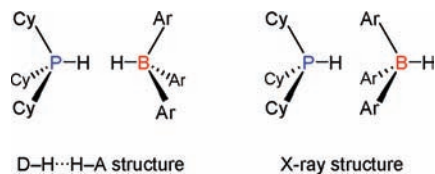
Figure 6. Calculated stabilization Gibbs free energies of the products of the hydrogen splitting reactions, plotted as a function of the reciprocal of the distance of the donor and acceptor atoms in the product ( $d_{DA}^{-1}$ ). Linear fit of linked systems corresponds to the Coulomb interaction of  $q$  point charges at distance  $d_{DA}$ .

previously in several reports,<sup>15,17,18,28,29,31–34</sup> may also contribute to the product stabilization. Indeed, we find rather short H...H contact distances ( $d_{H...H}$ ) in the equilibrium structures

(76) The gas-phase stabilization electronic energies of nonlinked systems show a notable linear correlation with  $d_{DA}^{-1}$ , underlining the importance of electrostatics (see Supporting Information). However, due to the small  $d_{DA}$  range, the damping effect of the solvent renders this correlation undetectable in the solvent-phase  $\Delta G_{stab}$  values.

of the  $[DH]^+[HA]^-$  species, typically in the 1.5–1.9 Å range, but interestingly, a correlation is also absent between the stabilization energies and  $d_{H...H}$  for the investigated systems.<sup>75</sup> These results suggest that the formation of dihydrogen bonds in  $H_2$  splitting processes is not a major factor for favorable energetics. This is further supported by the results obtained for two isomers of the  $[Cy_3PH]^+[HB(p-C_6F_4H)_3]^-$  product, which indicate that the structure characterized by a rather short





**Figure 7.** Two product isomers of  $[\text{Cy}_3\text{PH}]^+[\text{HB}(p\text{-C}_6\text{F}_4\text{H}_3)]^-$ .

dihydrogen bond ( $d_{\text{H}\cdots\text{H}} = 1.54 \text{ \AA}$ ) is notably less stable (by 4.5 kcal/mol) than that corresponding to the X-ray data.<sup>24</sup> In the latter structure, the P–H and B–H vectors are aligned into the same direction; however, the noncovalent  $\text{Cy}\cdots\text{aryl}$  contacts give rise to considerable stabilization (see Figure 7 as well as Figure S3 in Supporting Information).

Figure 6 reveals that the linked systems tend to have more favorable stabilization free energies than the nonlinked pairs, which can partly be attributed to the difference in the stoichiometry of the stabilization step (see Scheme 2). This step of the thermodynamic cycle involves entropy loss for nonlinked systems due to the ion association, whereas the number of molecules does not vary in the stabilization step of linked pairs. In the present partitioning, this step accounts for the different entropy changes of the overall reactions, which represents a fundamental difference between the two families of FLPs.<sup>77</sup>

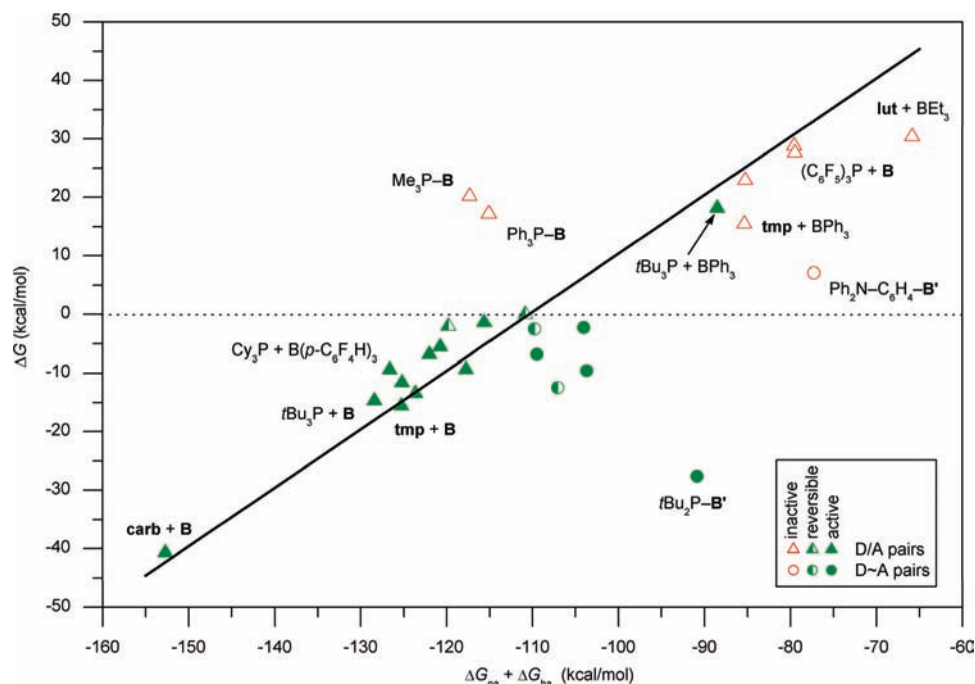
We furthermore find that the  $\Delta G_{\text{stab}}$  values of linked FLPs vary in a broader energy interval than those of the D/A pairs, and their trends are consistent with a simple electrostatic interpretation (see Figure 6). The directly linked  $t\text{Bu}_2\text{P}-\text{B}'$  molecule is of course a unique case owing to the short P–B distance; however, the Coulomb stabilization in the anticipated hydrogenation product of the *o*-phenylene bridged aminoborane ( $[\text{H}^+\text{PPh}_2\text{N}-\text{C}_6\text{H}_4-\text{B}'\text{H}^-]$ ) with  $d_{\text{NB}} = 2.88 \text{ \AA}$  is still significant. The stabilizing effect is reduced gradually with increasing intramolecular  $d_{\text{DA}}$  separations, and  $\Delta G_{\text{stab}}$  is calculated to be about  $-20$  to  $-25$  kcal/mol for *p*- $\text{C}_6\text{F}_4$ -linked products. One can conclude from these results that the intramolecular distance of the active sites has a significant and

well-defined effect on the acid–base cooperativity, and the variations in this term can easily exceed those found in the ion pair binding energies of nonlinked pairs.

**Assessment of the Role of Acid–Base Properties.** Inspecting the magnitude of the overall reaction free energies and their constituent terms, we see that all three negative contributions (proton attachment, hydride attachment, and stabilization terms) are essential to obtain exergonic hydrogenation processes. Among these factors, the acid–base properties are found to show the largest diversity for the series of investigated compounds. In order to correlate the cumulative acid–base strength of Lewis pairs with the thermodynamics of  $\text{H}_2$  splitting reactions, we plotted the overall reaction free energies as a function of  $\Delta G_{\text{pa}} + \Delta G_{\text{ha}}$  (see Figure 8).

The figure clearly demonstrates that for most of the nonlinked systems studied so far, the absence of the dative bond and the near invariance of the ion pair binding energy infers a decisive role for the donor–acceptor strength in determining the thermodynamic feasibility of  $\text{H}_2$  activation. Significant deviations from the linear relationship between  $\Delta G$  and  $\Delta G_{\text{pa}} + \Delta G_{\text{ha}}$  can be attributed either to the formation of dative bonds (e.g.,  $\text{Me}_3\text{P}-\text{B}$  and  $\text{Ph}_3\text{P}-\text{B}$ ) or to unusually large ion pair binding energies (e.g., **lut** +  $\text{BET}_3$  and **tmp** +  $\text{BPh}_3$ ), emphasizing the importance of these factors in particular cases. For the datively bound  $\text{Me}_3\text{P}-\text{B}$  and  $\text{Ph}_3\text{P}-\text{B}$  systems, the cumulative acid–base strengths are comparable to those obtained for several reactive pairs, but the  $\Delta G_{\text{prep}}$  terms lead to notable endergonicities.

For most of the reactive D/A pairs, the calculated  $\Delta G_{\text{pa}} + \Delta G_{\text{ha}}$  values fall between  $-110$  and  $-130$  kcal/mol and these systems are combinations of bulky P and N donors with strong Lewis acids (**B** or  $\text{B}(p\text{-C}_6\text{F}_4\text{H}_3)$ ). The reaction free energies for these D/A pairs are predicted to be between 0 and  $-15$  kcal/mol. The most exergonic systems in this group involve strong bases (**tmp** and  $t\text{Bu}_3\text{P}$ ) combined with **B**, which indicates that further electronic modifications in the perfluoroaryl groups of **B** can be carried out while still retaining the exergonic character



**Figure 8.** Overall Gibbs free energy of the reactions plotted as a function of the cumulative acid–base strength. The straight line was drawn using  $\Delta G_{\text{prep}} = 0$  and the mean  $\Delta G_{\text{stab}}$  of the nonlinked systems ( $-18.4$  kcal/mol).

of H<sub>2</sub> splitting reactions. The **carb** + **B** combination is characterized by particularly enhanced cumulative acid–base strength, which however suggests that bulky carbenes or analogous compounds might be used successfully to activate H<sub>2</sub> in conjunction with Lewis acceptors considerably less acidic than **B**. At the other limit of the  $\Delta G_{\text{pa}} + \Delta G_{\text{ha}}$  scale, the D/A pairs involve either boranes with significantly reduced acidities (BPh<sub>3</sub>, BMe<sub>3</sub> and BEt<sub>3</sub>), or the electron deficient (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>P phosphine, and accordingly, the H<sub>2</sub> splitting reactions are predicted to be thermodynamically unfavorable. As noted before, the calculated  $\Delta G = +18.2$  kcal/mol for the *t*Bu<sub>3</sub>P + BPh<sub>3</sub> pair, which belongs to this group of D/A pairs as well, contradicts with experimental findings.<sup>8</sup> The systematic trends revealed in our study for the reaction free energies and the agreement found for all other investigated reactions suggest that revision of the experimental data might be necessary in this particular case.

Although a much smaller number of linked systems were investigated in our study, a few general observations can be made from the data presented in Figure 8. As discussed above, lower entropic cost is associated with the hydrogen splitting in linked systems as compared to nonlinked pairs. As a consequence, smaller cumulative acid–base strength is generally sufficient to render a linked system thermodynamically feasible. This is apparent from the  $\Delta G_{\text{pa}} + \Delta G_{\text{ha}}$  values obtained for the reactive D~A systems, which are all between –110 and –90 kcal/mol. Another important observation is that no clear correlation between the overall free energy and the cumulative acid–base strength can be established for the investigated linked pairs, which is due to larger variations in the  $\Delta G_{\text{stab}}$  components as pointed out in the previous section. This feature provides an additional degree of freedom to control the thermodynamics of H<sub>2</sub> splitting reactions. It is interesting to note in this regard that the unreactive nature of the Ph<sub>2</sub>N–C<sub>6</sub>H<sub>4</sub>–**B'** system indeed stems from the low basicity of the N atom as pointed out by Piers et al.,<sup>53</sup> but despite the unfavorable acid–base properties, the calculated  $\Delta G = +7.1$  kcal/mol is surprisingly low owing to unusually high stabilization free energy. These results indicate that *o*-phenylene bridged donor–acceptor pairs could be promising candidates in future developments.

#### 4. Concluding Remarks

Since the discovery of the first systems based on the FLP concept, numerous transition metal free Lewis acid–base pairs capable of activating hydrogen have appeared in the literature, and even more are expected in the future. The aim of the work presented here was to contribute to the understanding of the

reactivity of recently reported FLPs with H<sub>2</sub> in terms of thermodynamics. We considered a series of experimentally described FLP systems and carried out quantum chemical calculations to characterize the energetics of the hydrogen activation reactions using density functional and continuum solvation methods. We also presented a partitioning of the reaction free energy that allows the separation of various influencing factors. The main conclusions drawn from our results can be summarized as follows:

(1) Among the systems we studied, the absence of reactivity toward H<sub>2</sub> originates from the unfavorable thermodynamics of the processes.

(2) Acidity, basicity, and product stabilization (either as ion pair binding energy or as intramolecular cooperativity) are all important aspects of these reactions that should be considered to overcome the energetic cost of the heterolytic H–H bond splitting and, in particular cases, the cleavage of the donor–acceptor bonds. The overall reaction energy is the result of these five terms, four of which can, in general, be tuned by varying the molecular structure.

(3) Nonlinked Lewis pairs that do not form dative bond in equilibrium show good correlation between cumulative acid–base strength and the overall reaction free energy due to the similar structure of the products. In contrast, the remarkable variation of the intramolecular cooperativity in linked systems may easily become a decisive factor in reactivity.

(4) Linked systems lose less entropy when reacting with H<sub>2</sub> than do unbound, nonlinked systems. As a consequence, smaller acid–base strength and stabilization may be sufficient to produce reactive compounds.

Besides favorable thermodynamics, kinetic requirements have to be fulfilled as well to ensure appropriate reactivity of the hydrogen-activating molecules. Yet we hope that our present results help in rationalizing the trends in the systems described so far and provide some guidance to future experimental studies. Further work devoted to cooperative Lewis acid–base systems is in progress in our laboratory.

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**Supporting Information Available:** Complete ref 49; Cartesian coordinates and absolute energies of all stationary points located on the potential energy surface; details concerning some parts of our work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(77) Eleven translational or rotational degrees of freedom are converted to internal motions in the  $D + A + H_2 \rightarrow [DH]^+[HA]^-$  reaction, while only five are affected in  $D\sim A + H_2 \rightarrow [^+HD\sim AH^-]$ .