### Frustrated Lewis Pairs

### Why Does the Intramolecular Trimethylene-Bridged Frustrated Lewis Pair Mes<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> Not Activate Dihydrogen?

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**Abstract:** The methyl labelled C<sub>3</sub>-bridged frustrated phosphane borane Lewis pair (P/B FLP) **2b** was prepared by treatment of Mes<sub>2</sub>PCI with a methallyl Grignard reagent followed by anti-Markovnikov hydroboration with Piers' borane [HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>)]. The FLP **2b** is inactive toward dihydrogen under typical ambient conditions, in contrast to the C<sub>2</sub>- and C<sub>4</sub>-bridged FLP analogues. Dynamic NMR spectroscopy showed

### Introduction

Frustrated Lewis pairs (FLPs) have undergone remarkable development in recent years. The combination of nonquenched bulky main group element based Lewis acids and bases has allowed the detection of a variety of cooperative reactions. Small molecule binding or activation, features usually attributed to transition metal containing systems, has become a prominent property of many such Lewis acid/Lewis base combinations.<sup>[1]</sup> Intramolecular FLPs have played an important role in this development.<sup>[2]</sup> The ethylene-bridged P/B FLP  $1 a^{[3]}$ (Scheme 1) and some of its derivatives, were shown to bind a variety of oxides of the elements carbon, nitrogen and sulfur<sup>[4]</sup> or to assist in their specific transformation.<sup>[5]</sup> The FLP 1 a has been one of the most active non-metallic dihydrogen activators.<sup>[6]</sup> It rapidly cleaves dihydrogen heterolytically and has served as a catalyst for the hydrogenation reaction of a variety of organic substrates.<sup>[7]</sup> We had a look at the homologues of the FLP 1a. The tetramethylene-bridged system 3a is readily available by means of a hydroboration reaction (see below). It was shown to be an active P/B FLP for the cleavage of dihydrogen under mild conditions.<sup>[8]</sup> In stark contrast to these re-

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-	chem.201505200

that this was not due to kinetically hindered P···B dissociation of **2b**. DFT calculations showed that the hydrogen-splitting reaction of the parent compound **2a** is markedly endergonic. The PH<sup>+</sup>/BH<sup>-</sup> H<sub>2</sub>-splitting product of **2b** was indirectly synthesized by a sequence of H<sup>+</sup>/H<sup>-</sup> addition. It lost H<sub>2</sub> at ambient conditions and confirmed the result of the DFT analysis.

sults is the behaviour of the trimethylene-bridged P/B system **2***a*, which was shown to be inactive towards dihydrogen under our typical reaction conditions.<sup>[9]</sup> So far we were not able to find reaction conditions where **2***a* was able to react with H<sub>2</sub>. We have investigated this at-first-sight strange difference of the behaviour of the FLPs **1** to **3** by a combined experimental/theoretical study and were able to arrive at an explanation for this dichotomy. This will be outlined in this article.



Scheme 1. Intramolecular P/B frustrated Lewis pairs.

### **Results and Discussion**

### The question of the strength of the P/B interaction

We had previously shown that the activation barrier of the P/B interaction in saturated vicinal P/B FLPs can be determined by dynamic <sup>19</sup>F NMR spectroscopy by using suitably substituted chiral derivatives.<sup>[10]</sup> A typical example is compound **1b** (Scheme 2) which contains a pair of carbon chirality centres with a defined relative configuration. The compound shows a mutual P···B interaction in the solid state. In solution it features a pair of diastereotopic C<sub>6</sub>F<sub>5</sub> ligands at boron at low temperature which undergo coalescence with increasing monitoring temperature due to rapidly increasing equilibration with the high lying open intermediate **1b** (open) which features a trigonal-planar boron coordination geometry with homotopic C<sub>6</sub>F<sub>5</sub> substituents. From the dynamic <sup>19</sup>F NMR spectra a Gibbs activation energy of  $\Delta G^{\pm}$  (298 K)=12.1(±0.3) kcal

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<b>Table 1.</b> Gibbs activation energies ( $\Delta G^*$ ) of P/B dissociation in the FLPs <b>1 b</b> to <b>3 b</b> . <sup>[a]</sup>				
	<b>1 b</b> <sup>[10a]</sup>	2 b	3 b	
$\Delta G^{+}$	12.1	14.5	12.8	
T <sub>coal</sub> [K]	298	310	285	
[a] $\Delta G^{\pm} = \pm 0.3$ kcalmol <sup>-1</sup> ; from dynamic <sup>19</sup> F NMR spectroscopy at $T_{coal}$ .				

 $mol^{-1}$  was calculated for the P…B dissociation in compound  $1\,b.^{\rm [10a]}$ 

We needed to determine the favoured structure of the trimethylene-bridged FLP **2**. At the same time it would be convenient to have a stereochemical label introduced that would allow determination of the P…B dissociation barrier by the NMR method. Therefore, we prepared the suitably labelled variant **2b** by the following synthetic route (Scheme 3). Dimesityl(methallyl)phosphane (**4a**) was prepared by the treatment of Mes<sub>2</sub>PCI with methallylmagnesium chloride. The phosphane **4a** was isolated as a white solid in 83% yield. It was characterized by C,H-elemental analysis and by NMR spectroscopy (<sup>31</sup>P:  $\delta = -24.8$  ppm, for further details see the Supporting Information).



Scheme 3. Formation of the FLP 2b.

Treatment of the methallylphosphane **4a** with one molar equivalent of Piers' borane  $[HB(C_6F_5)_2]^{[11]}$  resulted in a clean anti-Markovnikov hydroboration of the pendant C=C double bond to give the P/B product **2b**, which was isolated as a white amorphous solid in 87% yield. It was characterized by C,H-elemental analysis, by NMR spectroscopy and by X-ray diffraction (single crystals were obtained from toluene/pentane by the diffusion method). In the solid state compound **2b** shows a five-membered heterocyclic structure with a mutual P···B interaction (Figure 1). Both the phosphorus and the boron atom show tetra-coordination ( $\Sigma P1^{CCC} = 324.3$ ,  $\Sigma B1^{CCC} = 334.9$ ). The five-membered core is found in a nonplanar distorted twist conformation. Carbon atom C2 has the extra methyl group attached.



**Figure 1.** A view of the molecular structure of compound **2b** (the *R* enantiomer is depicted; thermal ellipsoids are set at 50% probability). Selected bond lengths [Å] and angles [ $^{\circ}$ ]: P1-C1 1.846(3), P1-B1 2.076(3), B1-C3 1.636(4), C3-C2 1.535(4), C2-C1 1.545(4), C1-P1-B1 94.3(1), C2-C3-B1 108.9(2), B1-C3-C2-C1 -54.0(3), C3-C2-C1-P1 22.1(2), B1-P1-C1-C2 8.8(2).

In solution ([D<sub>8</sub>]toluene) compound **2b** shows a broad  $^{11}$ B NMR signal at  $\delta\!=\!-3.5$  ppm at 213 K, typical of tetra-coordinated boron. The <sup>11</sup>B NMR chemical shift is practically temperature invariant between 213 and 299 K; the signal only gets sharper with increasing temperature. The <sup>31</sup>P NMR resonance was found at  $\delta =$  24.0 ppm (at 213 K). It also did not change much with temperature. In contrast, compound 2b showed temperature-dependent dynamic <sup>1</sup>H (see the Supporting Information) and <sup>19</sup>F NMR spectra. At low temperature (253 K) we observed four separate o-C<sub>6</sub>F<sub>5</sub> <sup>19</sup>F NMR signals, indicating hindered rotation of both diastereotopic C<sub>6</sub>F<sub>5</sub> groups around the B-C vector. In addition, at that temperature we monitored two equal intensity  $p-C_6F_5$  resonances and four  $m-C_6F_5$  signals. Increasing the temperature overcomes the barrier of rotation around the C-B bond and the barrier of P-B dissociation. The latter leads to pairwise equilibration of the ortho-, the paraand the meta- $C_6F_5$  resonances of the  $B(C_6F_5)_2$  substituent. From the coalescence of the pair of  $p-C_6F_5$  <sup>19</sup>F NMR signals we have estimated the Gibbs activation energy of the P-B dissociation in the trimethylene-bridged P/B FLP **2b** as  $\Delta G^{\dagger}$  (310 K) = 14.5( $\pm$ 0.3) kcal mol<sup>-1</sup>.



Scheme 2. Activation barrier of the P-B dissociation in the FLP 1 b.

We exposed the FLP **2b** to dihydrogen (for details see the Supporting Information) but could not observe any formation of the respective dihydrogen splitting product. However, the system **2b** reacted with the strongly  $\sigma$ -donating Arduengo-carbene **5**.<sup>[12]</sup> Treatment of the P/B FLP **2b** with the N-heterocyclic carbene **5** went to completion within 30 min at ambient temperature in benzene. Workup eventually gave the product **6** as



a white solid in 70% yield. It showed a <sup>31</sup>P NMR signal at  $\delta = -25.7$  ppm and an <sup>11</sup>B NMR resonance at  $\delta = -14.0$  ppm. The <sup>1</sup>H NMR spectrum of the [B]-NHC unit shows hindered rotation around the B-C and N-C vectors which results in observation of a total of six mesityl methyl signals and four CH methine resonances of this unit at 299 K. We observe the <sup>19</sup>F NMR signals of a pair of diastereotopic C<sub>6</sub>F<sub>5</sub> substituents at boron. It shows the <sup>1</sup>H NMR features of a pair of diastereotopic mesityl groups at phosphorus and the high field <sup>1</sup>H NMR resonance of the methyl group at the C<sub>3</sub>-bridge.

Single crystals of compound **6** suitable for the X-ray crystal structure analysis were obtained from dichloromethane. The structure shows that the P···B bond was cleaved and the N-heterocyclic carbene ligand attached to the boron atom (Figure 2). The C<sub>3</sub>-bridge in compound **6** has attained a conformation that results in a maximal spatial separation of the pair of heteroatom based functional groups. The boron atom shows a pseudotetrahedral coordination geometry; the phosphorus coordination geometry is trigonal-pyramidal ( $\Sigma P1^{CCC} = 314.7$ ).



**Figure 2.** Molecular structure of the N-heterocyclic carbene addition product **6** (thermal ellipsoids are set at 30% probability). Selected bond lengths [Å] and angles [°]: P1-C1 1.858(4), C1-C2 1.541(6), C2-C3 1.547(5), C3-B1 1.638(6), C5-B1 1.683(6), C2-C1-P1 110.6(3), C1-C2-C3 108.7(3), C2-C3-B1 120.8(3), C3-B1-C5 110.3(3), P1-C1-C2-C3 164.3(3), C2-C3-B1-C5 175.3(3).

We prepared the tetramethylene-bridged P/B FLP **4b** for comparison and chose a synthesis that resulted in the introduction of a stereochemical label at carbon atom C3 in order to allow the determination of the rate of P--B rupture by the dynamic NMR method analogously as described above.

Dimesitylphosphorus chloride was treated with the respective Grignard reagent to give the alkenylphosphane **4b**, isolated as a crystalline solid in 55% yield (Scheme 4). The compound was characterized by C,H-elemental analysis, by X-ray diffraction (see the Supporting Information for details, including a projection of the molecular structure) and by spectroscopy (<sup>31</sup>P NMR:  $\delta = -18.6$  ppm; <sup>1</sup>H NMR:  $\delta = 4.70$ , 4.68 ppm, = CH<sub>2</sub>). Treatment of **4b** with HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (one molar equiv) in toluene at r.t. (30 min) gave the hydroboration product **3b** that was isolated from the workup procedure as a white solid in 80% yield.

The X-ray crystal structure analysis shows 1,4-attachment of the PMes<sub>2</sub> and  $B(C_6F_5)_2$  groups at the saturated  $C_4$ -bridge



Scheme 4. Formation and chemical features of the FLP 3b.



**Figure 3.** A view of the molecular structure of compound **3b** (thermal ellipsoids are set at 30% probability). Selected bond lengths [Å] and angles [°]: P1-C1 1.848(1), P1-B1 2.093(1), C1-C2 1.538(2), C2-C3 1.522(2), C3-C4 1.532(2), C4-B1 1.640(2), C1-P1-B1 102.0(1), C2-C1-P1 122.3(1), C3-C4-B1 116.1(1), B1-P1-C1-C2 -33.7(2), C1-P1-B1-C4 46.4(1), C1-C2-C3-C4 -45.5(2).

(Figure 3). Carbon atom C3 bears the methyl substituent. We note a marked phosphorus-boron interaction; the P1...B1 bond length in both the compounds **2b** and **3b** are almost identical. In **3b** both the phosphorus and the boron atom show pseudotetrahedral coordination geometries.

In solution (CD<sub>2</sub>Cl<sub>2</sub>) compound **3b** shows an <sup>11</sup>B NMR signal at  $\delta\!=\!-5.0~{
m ppm}$  (233 K) and a  $^{31}{
m P}\,{
m NMR}$  resonance at  $\delta\!=\!$ 1.7 ppm (233 K). These resonances are practically temperature invariant in the 233 to 299 K temperature range. Compound 3b shows a similar dynamic behaviour as described for 2b. At 253 K (and below) compound 3b shows ten separate <sup>19</sup>F NMR signals of the pair of C<sub>6</sub>F<sub>5</sub> groups at boron, belonging to four o-, two p- and four  $m-C_6F_5$  fluorine substituents (Figure 4). This indicates a P---B interacting structure (just as observed by X-ray diffraction in the solid state) and "frozen" rotation of both the C<sub>6</sub>F<sub>5</sub> groups around the B-C vectors at these conditions on the <sup>19</sup>F NMR time scale. Increasing the monitoring temperature resulted in coalescence of each the four o-C<sub>6</sub>F<sub>5</sub> signals, the pair of  $p-C_6F_5$  resonances and the four  $m-C_6F_5$  signals, eventually leading to a simple <sup>19</sup>F NMR spectrum of **3b** at high temperature that showed only three coalesced signals in a 2:1:2 intensity ratio, originating from the o-, p- and m-C<sub>6</sub>F<sub>5</sub> fluorine atoms



Figure 4. Temperature-dependent dynamic <sup>19</sup>F NMR (470 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectra of compound 3 b.

(Figure 4). This behaviour indicated two dynamic processes almost equally becoming facile with increasing temperature that resulted in coalescence of the respective NMR signals, namely onset of  $C_6F_5$  group rotation around the B–C bonds and P…B opening and closing becoming rapid on the <sup>19</sup>F NMR time scale. From the coalescence of the pair of p- $C_6F_5$  resonances we estimated the Gibbs-activation energy of the equilibration of the global minimum structure of **3 b** with its high lying **3 b**(open) isomer as  $\Delta G^+(280 \text{ K}) = 12.8(\pm 0.3) \text{ kcal mol}^{-1}$ .

The C<sub>4</sub>-bridged FLP **3b** was exposed to dihydrogen at near to ambient conditions (r.t., 1.5 bar H<sub>2</sub>, 16 h). This resulted in an about 50% conversion to the dihydrogen splitting product **7b**, which was characterized spectroscopically from the reaction mixture. It showed the characteristic [P]-H <sup>1</sup>H NMR signal at  $\delta$ =7.60 ppm with the large <sup>1</sup>J<sub>PH</sub>  $\approx$  475 Hz coupling constant (<sup>31</sup>P NMR:  $\delta$ =-9.2 ppm) and an <sup>11</sup>B NMR resonance at  $\delta$ = -21.7 ppm with <sup>1</sup>J<sub>BH</sub>  $\approx$  86 Hz [in addition to the respective heteroatom signals of the remaining compound **3b** (<sup>31</sup>P:  $\delta$ = 1.8 ppm, <sup>11</sup>B:  $\delta$ =-2.8 ppm in CD<sub>2</sub>Cl<sub>2</sub> at 299 K)].

The analogous reaction was carried out with D<sub>2</sub> to give **7 b**-D<sub>2</sub>. We monitored a <sup>31</sup>P NMR 1:1:1 intensity triplet of the [P]-D moiety at  $\delta = -9.5$  ppm (<sup>1</sup>J<sub>PD</sub>=72.6 Hz) and a broad <sup>11</sup>B NMR resonance at  $\delta = -22.0$  ppm, again in the presence of the <sup>31</sup>P/ <sup>11</sup>B NMR resonances of the starting material **3 b**. The <sup>2</sup>H NMR spectrum of compound **7 b**-D<sub>2</sub> showed signals at  $\delta = 7.62$  ppm ([P]-D) and  $\delta = 2.76$  ppm ([B]-D), respectively.

The FLP **3b** turned out to be a reasonably active metal-free hydrogenation catalyst for some bulky imines<sup>[13]</sup> and an enamine<sup>[7]</sup> (Scheme 5). Some slow and incomplete catalytic conversion of the imines **8a,b** to the respective *sec*-amines and the enamine **10** to the corresponding *tert*-amine could be achieved at close to normal conditions (1.5 bar H<sub>2</sub>, r.t., 20 h, 10 mol% of **3b**). With 30 bar H<sub>2</sub> pressure complete imine hydrogenation was achieved at r.t. within 20 h with 5 mol% of **3b**. Similarly, the enamine was completely hydrogenated



Scheme 5. Catalytic hydrogenation reactions.

under more forcing conditions at the **3b** catalyst (5 mol%; for further details see the Supporting Information).

Our study has shown that the three oligomethylene-bridged  $Mes_2P-(CH_2)_n-B(C_6F_5)_2$  FLPs react differently with dihydrogen. Compounds 1a,b split dihydrogen very rapidly and have served as metal-free catalysts for the hydrogenation of a variety of substrates. The tetramethylene-bridged system 3a is also an active dihydrogen splitting FLP; however, dihydrogen splitting by its methyl-substituted derivative **3b** is not complete but arrives at about 1:1 equilibrium. The trimethylene-bridged system 2b does not split dihydrogen under our typical reaction conditions. The dynamic NMR study has shown that this is probably not due to a total inhibition of the necessary P-B dissociation. The P-B cleavage in 2b shows a by about 2 kcal mol<sup>-1</sup> higher dissociation barrier as compared to its relatives 1b and 3b, respectively. However, this still represents a fast opening (and closing) situation of the P-B unit. Consequently, we could trap the 2b (open) form with an N-heterocyclic carbene. We conclude, that unfavourable kinetics of the generation of the active open FLP isomer is not likely to be the reason for the observed inactivity of the FLPs 2a,b toward di-

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hydrogen in contrast to **1 a,b** or **3 a,b**. There must be another reason.

## DFT analysis of the systems 1, 2 and 3 and their reaction with dihydrogen

We investigated the reaction profile of the trio of the parent ethylene-, trimethylene- and tetramethylene-bridged P/B FLPs **1a**, **2a**, and **3a** with density functional theory (DFT) calculations. All the structures were fully optimized at TPSS level of theory,<sup>[14]</sup> with the BJ-damped variant of the DFT-D3 dispersion correction<sup>[15]</sup> in conjunction with the def2-TZVP basis set.<sup>[16]</sup> Accurate electronic energies were obtained from single-point calculations at the PW6B95-D3 level<sup>[17]</sup> with a basis set of def2-TZVP, and the solvation Gibbs free energies were computed by employing COSMO-RS (conductor-like screening model for real solvents) solvation model<sup>[18]</sup> (for details, see the Supporting Information).

A previous DFT study<sup>[19]</sup> that we had carried out had shown that the ethylene-bridged P/B FLP **1 a** equilibrated with a reactive open *gauche*-form that effected heterolytic cleavage of dihydrogen in a concerned fashion with a distorted chair-shaped six-membered transition state. The active P/B FLP isomer **1 a** (open) was located by our DFT calculation about 9 kcalmol<sup>-1</sup> above the global **1 a** minimum (Figure 5, left). From our kinetic study (dynamic <sup>19</sup>F NMR, see above) we knew that **1 a** (open) was populated by a rapid pre-equilibrium ( $\Delta G^+ \approx 12$  kcalmol<sup>-1</sup>), to be followed by rate determining H<sub>2</sub>-cleavage [transition state calculated about 9 kcalmol<sup>-1</sup> above **1 a** (open)] to give the respective zwitterionic Mes<sub>2</sub>PH<sup>+</sup>-CH<sub>2</sub>CH<sub>2</sub>BH<sup>-</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> product. The overall dihydrogen splitting reaction at the FLP **1 a** is strongly exergonic by -7.6 kcalmol<sup>-1</sup>.

The energy profile of the reaction of the tetramethylenebridged P/B FLP with dihydrogen looks similar. The rapid preequilibrium generates the intermediate **3a** (open) (+10.4 kcal mol<sup>-1</sup>) which then rapidly reacts via transition state **TS 3a** (+



**Figure 5.** Left: PW6B95-D3/def2-TZVP//TPSS-D3/def2-TZVP energy profiles of the  $H_2$ -splitting reactions of: a)  $C_2$ -bridged FLP **1 a**, b)  $C_3$ -bridged FLP **2 a**, and c)  $C_4$ -bridged FLP **3 a**. Notations used: **CLO** for closed isomer, **OPE** for open isomer, **TS** for transition state, and **PD** for hydrogenated product. Right: fully optimized (TPSS-D3/def2-TZVP) transition states (**TS**) for  $H_2$  activation by FLP **1 a** to **3 a**. The hydrogen atoms are omitted for clarity, except  $H_2$  molecules. Colour legend: P yellow, B pink, F green, C black and H white. For closed isomers (**CLO**), open isomers (**OPE**) and hydrogenated products (**PD**), see Supporting Information.

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13.2 kcal mol<sup>-1</sup> above **3 a** (open); Figure 5, right) to give the H<sub>2</sub>-splitting product Mes<sub>2</sub>PH<sup>+</sup>-(CH<sub>2</sub>)<sub>4</sub>-BH<sup>-</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**7 a**, that is, **PD 3 a**). In this case the overall reaction is slightly endergonic (+ 1.5 kcal mol<sup>-1</sup>) which is qualitatively in accord with our finding of a reversible H<sub>2</sub>-splitting reaction of the methyl-substituted analogue **3 b** (see above).

According to the DFT calculation the overall appearance of the reaction profile of the  $\mathbf{2} + H_2$  reaction is similar: the rapid pre-equilibrium generates the P/B dissociated isomer  $\mathbf{2a}$  (open; +14.6 kcalmol<sup>-1</sup>). The calculated barrier of the subsequent H<sub>2</sub>-splitting reaction is a little higher [+11.1 kcalmol<sup>-1</sup> above  $\mathbf{2a}$  (open)] than found for the ethylene-bridged P/B FLP **1a**, but lower than tetramethylene-bridged P/B FLP **3a**. However, in contrast to the other two examples the formation of the hydrogen splitting product Mes<sub>2</sub>PH<sup>+</sup>-(CH<sub>2</sub>)<sub>3</sub>-BH<sup>-</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**11a**; i.e., **PD 2a**) in this case is markedly endergonic (+8.6 kcalmol<sup>-1</sup>).<sup>[20]</sup>

We conclude that our DFT analysis has revealed the reason for the different behaviour of the trimethylene-bridged P/B FLP system **2** as opposed to its ethylene- or tetramethylenebridged neighbours: this is due to a thermodynamic effect. In solution both the  $H_2$ -splitting reactions by the FLPs **1** and **3** are overall exergonic or slightly endergonic, but the trimethylene-bridged system **2** here in question, is markedly endergonic and, therefore, is not observed under our typical  $H_2$ -splitting conditions.

# Experimental confirmation of the endothermicity of the H<sub>2</sub>-splitting product 11 b at the trimethylene-bridged P/B FLP core

Since we could not prepare the H<sub>2</sub>-splitting product **11 b** by reacting the P/B FLP **2 b** with dihydrogen, we decided to attach a proton and a hydride in two consecutive steps. We employed a procedure that we had used before.<sup>[21]</sup>

Trifluoromethane sulfonic acid was slowly added to the P/B FLP **2b** in dichloromethane at r.t. Workup eventually gave the phosphonium/borane triflate **12b** as an amorphous solid in 81% yield. Compound **12b** features a set of typical [P]H<sup>+</sup> resonances (<sup>1</sup>H NMR:  $\delta$ =7.69 ppm, <sup>1</sup>J<sub>PH</sub>≈473 Hz; <sup>31</sup>P:  $\delta$ = -17.9 ppm) and we have monitored the typical <sup>19</sup>F NMR resonance of the newly introduced -OSO<sub>2</sub>CF<sub>3</sub> group ( $\delta$ = -79.0 ppm) at boron (Scheme 6).

The X-ray crystal structure analysis of compound **12b** (Figure 6, single crystals were obtained from a dichloromethane solution at -40 °C) showed the presence of the triflate group



Scheme 6. Independent synthesis of the zwitterionic product 11 b.

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**Figure 6.** Molecular structure of the phosphonium/boron triflate compound **12b** (thermal ellipsoids are set at 30% probability). Selected bond lengths [Å] and angles [°]: P1-C1 1.811(2), B1-O1 1.603(3), B1-C3 1.607(4), C1-C2 1.545(3), C2-C3 1.546(3), C2-C1-P1 112.4(2), O1-B1-C3 108.5(2), C2-C3-B1 120.4(2), P1-C1-C2-C3 - 167.0(2), C1-C2-C3-B1 65.3(3), O1-B1-C3-C2 - 76.3(3).

attached at boron and the opened P/B FLP framework ( $\Sigma$ P1<sup>CCC</sup> = 342.5(1)).

The hydrocarbyl framework of compound **12b** shows a conformational antiperiplanar ( $\theta$  P1-C1-C2-C3  $-167.0(2)^{\circ}$ )/gauche ( $\theta$  C1-C2-C3-B1 65.3(3)°) arrangement.

We then exchanged triflate at boron for hydride. This was effected by treatment of the triflate 12b with chlorodimethylsilane at r.t. The reaction was carried out in a Young NMR tube and the reaction was followed by NMR spectroscopy over a period of about 2 days. After the addition of Me<sub>2</sub>Si(H)Cl to compound 12b in CD<sub>2</sub>Cl<sub>2</sub> at r.t. we directly observed a gas evolution. Nevertheless, <sup>1</sup>H NMR spectroscopy revealed that the PH<sup>+</sup>/BH<sup>-</sup> product **11b** had apparently been formed. We have monitored the signals of **11b** and **2b** in a about 1:1 ratio. Compound 11b shows a  $^{\rm 31}{\rm P}\,{\rm NMR}$  doublet in  ${\rm CD}_2{\rm Cl}_2$  at  $\delta\!=$ -16.2 ppm ( ${}^{1}J_{\rm PH} \approx$  479 Hz) ( ${}^{1}$ H:  $\delta$  = 7.83 ppm) [of **2b**:  ${}^{31}$ P  $\delta$  = 23.6 ppm] and an  $^{11}\mathrm{B}$  signal at  $\delta\!=\!-22.2$  ppm (  $^{1}\!J_{\rm BH}\!\approx\!86$  Hz). We have monitored the  ${\rm ^{19}F}\,\rm NMR$  signals of the pair of diastereotopic  $C_6F_5$  substituents of compound **11b** at boron at  $\delta =$ -133.3, -133.8 ppm (o),  $\delta = -164.7$ , -164.9 ppm (p) and  $\delta =$ -167.0, -167.2 ppm (m). After standing for 2 d at r.t. the dehydrogenation of the PH<sup>+</sup>/BH<sup>-</sup> product **11 b** under these conditions was complete and we only observed the characteristic NMR signals of the P/B FLP 2b (the spectra are depicted in the Supporting Information). We carried out a second experiment at 0°C and were actually able to isolate compound 11b reasonably pure. We then observed the cleavage of dihydrogen at r.t. with formation of 2b (for details see the Supporting Information).

### Conclusions

Our study has led us to a likely solution of the initial question. It seems that we have found an explanation for the difference of behaviour between the FLPs **2a**,**b** versus **1a**,**b** and **3a**,**b** toward dihydrogen. We have found that all three types of compounds show a marked P…B interaction in their global minimum structures, but all three open and close rapidly to generate the respective reactive open P/B FLP intermediates in



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low activation barrier pre-equilibrium steps. The activation of neither of these systems is kinetically problematic. Our DFT study has revealed that the observed differences in FLP behaviour are most likely thermodynamic in origin. It was shown that the overall hydrogen splitting reaction of the trimethylene FLP **2a** is markedly endergonic, in contrast to the slightly endergonic reaction of the compound **3a** and the exergonic reaction of **1a** with dihydrogen. This computational result was confirmed by an alternative stepwise synthesis of the formal hydrogen-splitting product **11b**, which was shown to completely lose H<sub>2</sub> at r.t. as expected for an endothermic compound.

This study served to solve a rather specific problem in FLP chemistry. However, at the same time its result pointed to a rather general feature of this chemistry and has reminded us to check for the thermodynamics of any of the reactions of the many new FLP systems when an apparent lack of reactivity or some unusual reaction branching is observed.<sup>[22]</sup> Often the kinetic feasibilities do not seem to pose any problems but specific thermodynamic features might in some cases pose serious restrictions. We hope that these findings will be helpful in the current rapid development of frustrated Lewis pair chemistry.

### **Experimental Section**

### Synthesis and characterisation

**Synthesis of 4a**: 2-Methylallylmagnesium chloride (12.00 mL, 6.00 mmol, 1.25 equiv) was added to a solution of dimesitylchlorophosphane (1.46 g, 4.80 mmol, 1.00 equiv) in tetrahydrofuran (20 mL) at 0°C. The reaction mixture was stirred at ambient temperature for 3 h, before all volatiles were removed in vacuo. The residue was redissolved in pentane (30 mL) and the resulting suspension was filtered via cannula (Whatman glass fibre filter). The colourless filtrate was dried in vacuo to give compound **4a** as a powdery white solid (1.35 g, 4.2 mmol, 83%). Elemental analysis calcd (%) for C<sub>22</sub>H<sub>29</sub>P: C 81.44, H 9.01; found: C 81.20, H 9.68.

Synthesis of 4b: 1st Step: Generation of the Grignard-reagent: Powdered magnesium (0.6 g, 25.0 mmol, 1.0 equiv) was suspended in tetrahydrofuran (50 mL) under an argon atmosphere in a dried three-necked round-bottom flask with reflux condenser. A solution of 4-bromo-2-methyl-1-butene (3.7 g, 25.0 mmol, 1.0 equiv) in tetrahydrofuran (40 mL) was added dropwise using an addition funnel. The reaction mixture was refluxed for 4 h and then stirred for another 16 h at room temperature. A conversion to the Grignard-reagent of 100% was assumed for the calculation of the stoichiometry in the next step. 2nd Step: Preparation of dimesityl(3methylbut-3-en-1-yl)phosphane: A solution of dimesitylchlorophosphane (6.1 g, 20.0 mmol, 0.8 equiv) in tetrahydrofuran (60 mL) was added dropwise at 0°C to the Grignard-solution and stirred for 20 h at ambient temperature. All volatiles were removed in vacuo and pentane (120 mL) was added to the sticky yellow residue. The pale yellow suspension was filtrated via cannula (Whatman glass fibre filter) and the obtained filtrate was dried in vacuo to give a pale yellow oil. The oil was purified by column chromatography (silica:  $CH_2CI_2:CyH = 3:10$ ;  $R_f$ : 0.44) to give a white, crystalline solid (3.6 g, 10.7 mmol, 55%). Crystals suitable for the X-ray crystal structure analysis were obtained from a dichloromethane solution of compound 4b. Elemental analysis calcd (%) for C<sub>23</sub>H<sub>31</sub>P: C 81.62, H 9.23; found: C 81.32, H 8.93.

**Synthesis of 2 b:** A solution of phosphane **4a** (100.0 mg, 0.3 mmol, 1.0 equiv) in toluene (1 mL) was added dropwise to a solution of Piers' borane [HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (106.6 mg, 0.3 mmol, 1.0 equiv) in toluene (2 mL) and stirred at r.t. for 30 min. The suspension was filtered through glass fibre filter (Whatman), all volatiles of the filtrate were removed in vacuo and the residue was washed with pentane (4× 2 mL). After being dried in vacuo for 6 h compound **2b** was obtained as a powdery white solid (178.7 mg, 0.3 mmol, 87%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane into a solution of compound **2b** in toluene. Elemental analysis calcd (%) for  $C_{34}H_{30}BF_{10}P$ : C 60.92, H 4.51; found: C 60.24, H 4.36.

**Synthesis of 3b**: A solution of phosphane **4b** (300.0 mg, 0.9 mmol, 1.0 equiv) in toluene (2 mL) was added dropwise to a solution of Piers' borane [HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (306.6 mg, 0.9 mmol, 1.0 equiv) in toluene (3 mL) and stirred at r.t. for 30 min. Then all volatiles were removed in vacuo and the obtained residue redissolved in pentane (5 mL). The solution was stored at -30 °C for 16 h. The pentane was removed with a pipette and the white solid was washed with pentane (4×2 mL). After drying the solid in vacuo for 4 h compound **3b** was obtained as a powdery white solid (488.6 mg, 0.5 mmol, 80%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane into a solution of compound **3b** in toluene at -35 °C. Elemental analysis calcd (%) for  $C_{35}H_{32}BF_{10}P$ : C 61.42, H 4.71; found: C 61.38, H 4.68.

**Synthesis of 6**: Compound **2b** (32.1 mg, 0.048 mmol, 1.0 equiv) was treated with 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (**5**; 14.6 mg, 0.048 mmol, 1.0 equiv) in benzene (2 mL) at r.t. for 30 min. Then all volatiles were removed in vacuo and the obtained white solid was washed with pentane (2×2 mL). After being dried in vacuo, compound **6** was obtained as a powdery white solid (34.2 mg, 0.035 mmol, 70%). Crystals suitable for the X-ray crystal structure analysis were obtained from a dichloromethane solution of compound **6**. Elemental analysis calcd (%) for C<sub>55</sub>H<sub>54</sub>BF<sub>10</sub>N<sub>2</sub>P: C 67.77, H 5.58, N 2.87; found: C 66.51, H 5.82, N 2.74.

Synthesis of 11 b: A solution of chlorodimethylsilane (210.0 mg, 247.5  $\mu$ L, 2.2 mmol, 5.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was added to a solution of compound 12 b (369.0 mg, 0.4 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) at -78 °C. The reaction mixture was warmed to 0 °C and stirred for 3 h at that temperature, before pentane (15 mL) was added at -78 °C. The solution was stored at -35 °C for 16 h and the suspension filtered through a glass fibre filter (Whatman). The resulting solid was washed with pentane (3×3 mL) at -78 °C and then dried in vacuo to give a white powdery solid (247.1 mg, 0.37 mmol, 82%).

**Synthesis of 12b**: A solution of compound **2b** (200.0 mg, 0.30 mmol, 1.0 equiv) in dichloromethane (2.0 mL) was added dropwise to a solution of triflic acid (44.4 mg, 25.8  $\mu$ L, 0.30 mmol, 1.0 equiv) in dichloromethane (2.0 mL) at room temperature in a Schlenk flask. The reaction mixture was stirred for 30 min at room temperature and then all volatiles were removed in vacuo. The resulting white solid was washed with pentane (8×2 mL) and dried in vacuo to give a white powdery solid (200.4 mg, 0.24 mmol, 81%). Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **12b** in dichloromethane at -40 °C. Elemental analysis calcd (%) for C<sub>33</sub>H<sub>31</sub>BF<sub>13</sub>O<sub>3</sub>PS: C 51.24, H 3.81; found: C 51.07, H 3.66.

### Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft and the European Research Council is gratefully acknowl-

Chem. Eur. J. 2016, 22, 5988 – 5995

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edged. The work of S.G. and L.L. was supported by the DFG in the framework of the "Gottfried-Wilhelm-Leibniz" prize.

**Keywords:** boron · density functional calculations dihydrogen activation · frustrated Lewis pair · phosphorus

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Received: December 30, 2015 Published online on March 21, 2016

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