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Frustrated Lewis Pair Behavior of an Open, Noninteracting Phosphane/Borane Pair at a Rigid Organic Framework: Exploring Decisive Factors for FLP Activity

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Supporting Information

ABSTRACT: The open, noninteracting vicinal P/B frustrated Lewis pair (FLP) at the very rigid, dibenzobicyclo[2.2.2]octadiene ("semi-triptycene") framework shows a trans 1,2-arrangement of the Mes₂P– and $(C_6F_5)_2B$ – Lewis base/Lewis acid pair. It is an active dihydrogen splitting reagent and shows a great variety of typical frustrated Lewis pair reactions under mild reaction conditions. This includes the 1,1-addition reaction to nitric oxide (NO) to form a persistent FLPNO[•] nitroxide radical as well as CO reduction by Piers' borane [HB(C_6F_5)₂] at the reactive FLP template. The new FLP undergoes thermodynamically favorable 1,4-addition reactions to 1,2-diketones. Most products were characterized by X-ray diffraction, and the 1,4-diketone addition reaction was analyzed by DFT calculation. A comparison with the internally interacting "parent" vicinal Mes₂PCH₂CH₂B(C_6F_5)₂ system revealed some decisive indications for very active FLPs.

INTRODUCTION

Intramolecular Lewis acid/Lewis base pairs have played a significant role in the development of frustrated Lewis pair (FLP) chemistry.¹ From early on, some such systems have exhibited high reactivities in small-molecule binding and/or activation.^{2,3} In order to serve as active FLPs, the Lewis acid/ base combinations must not be hindered from their cooperative action by any LA/LB adduct formation.⁴ This is often not the case in intramolecular systems.^{5,6} They often show global minimum structures that indicate some direct Lewis adduct formation. In order to show cooperative FLP behavior, the LA/ LB pair must dissociate in a preequilibrium step in order to become active. Fortunately, for many intramolecular FLPs adduct formation is weak. Nevertheless, the endergonic LA-LB \rightleftharpoons LA+LB equilibrium becomes part of the overall kinetic expression of FLP action and principally reduces the rate of FLP small-molecule reactions. Scheme 1 shows a typical example.

Geometric features and steric hindrance may make the LA/ LB interaction in intramolecular FLPs impossible and eliminate the preequilibrium situation altogether. The FLPs 3-5 depicted in Scheme 1 are some typical examples.^{4,8} The geometrically constrained noninteracting P/B systems 3 and 4 are rather reactive frustrated Lewis pairs; however, they are not well suited for a direct comparison with 1 because compound 3 shows an unsymmetrical environment of the Lewis acid/base pair and compound 4 is unstable with regard to isomerization. We recently found that the N/B pair 5 is an excellent acceptor for the H⁺/H⁻ pair from the dihydrogen activation product 2 and can, therefore, not be used reliably for the competition



Scheme 1. Examples of Interacting and Noninteracting FLPs



experiment.^{4b} We have now prepared a new open, noninteracting vicinal P/B FLP at the very rigid symmetrical dibenzobicyclo[2.2.2]octadiene framework. Our system contains a trans-1,2-attachment of the reactive $-PMes_2/-B(C_6F_5)_2$ pair. In this paper, we will describe the formation, characterization, and chemistry of this very rigid new member of the intramolecular FLP family of compounds and compare its typical FLP action with the internally interacting "parent" Mes_PCH_2CH_2B(C_6F_5)_2 FLP 1.⁷

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RESULTS AND DISCUSSION

Synthesis of the New P/B FLP System. The synthesis of the trans-1,2-P/B FLP 8 was carried out by a synthetic sequence that followed the reported preparation of the diphenylphosphino analogue of our $-PMes_2$ phosphane starting material 7.⁹ That in turn was prepared starting from dimesitylphosphinoacetylene (HC=C-PMes₂), which was oxidized to the respective acetylenic phosphinoxide HC≡C− $P(O)Mes_2$. This we used as a potent dienophile for the Diels-Alder reaction with anthracene (200 °C, 48 h in toluene in an autoclave) to give the dibenzobicyclo[2.2.2]octatrienylphosphinoxide 6, which we isolated as a solid in 84% yield after chromatographic purification (³¹P NMR: δ +24.9). The phosphinoxide 6 was then reduced to the respective alkenyldimesitylphosphane with trichlorosilane/ triethyl phosphite (50 °C, 48 h), according to a literature procedure,⁹ to give compound 7 as a yellow solid in 75% after chromatography. The phosphane was characterized by C,H elemental analysis, by spectroscopy [³¹P NMR δ -27.7, ¹H NMR δ 5.06 (³ J_{PH} = 7.4 Hz) (1-H), δ 6.53 (3-H), δ 5.10 (⁴ J_{PH} = 1.1 Hz (4-H), and by X-ray diffraction (for the X-ray crystal structure analysis and spectroscopic details, see the Supporting Information)

The hydroboration reaction of the alkenylphosphane with Piers' borane $[HB(C_6F_5)_2]^{10}$ went smoothly and gave the P/B FLP 8 as a yellow solid in 78% yield after workup (see Scheme 2). Single crystals of compound 8 were obtained from a

Scheme 2. Synthesis of the Noninteracting P/B FLP 8



solution in 1/5 (v/v) dichloromethane/pentane at -30 °C. The X-ray crystal structure analysis (see Figure 1) shows the formation of the doubly functionalized "semi-triptycene"¹¹ framework. The saturated section of the molecule has a pair of bulky PMes₂ and B(C₆F₅)₂ substituents attached to it. These substituents are found trans attached at the C2–C3 carbon– carbon single bond, as was expected from the regio- and stereoselective hydroboration reaction. The dihedral angle between the C2–P1 and C3–B1 vectors amounts to $\theta(P1-C2-C3-B1) = -106.0(4)^{\circ}$. Consequently, the boron atom features a trigonal-planar coordination geometry ($\Sigma B1^{CCC} = 359.0^{\circ}$) with both C₆F₅ substituents oriented slightly to the outside. The phosphorus atom shows the typical distorted-trigonal-pyramidal geometry with $\Sigma P1^{CCC} = 321.6^{\circ}$. The P1–B1 separation in compound 8 amounts to 3.964 Å.

The NMR spectra of compound 8 were obtained from our in situ prepared sample in d_2 -dichloromethane. It shows a ¹¹B NMR resonance at δ 74.7 and three ¹⁹F NMR signals (at 299 K) of the *o*,*p*,*m*-fluorine nuclei of the pair of C₆F₅ groups at boron with a large $\Delta^{19}F_{m,p} = 11.7$ ppm chemical shift difference.



Figure 1. Molecular structure of the open, noninteracting P/B FLP 8 (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): P1–C2 1.901(4), C1–C2 1.589(5), C2–C3 1.577(5), C3–C4 1.613(5), C3–B1 1.546(6); C1–C2–P1 107.6(2), C1–C2–C3 108.1(3), C2–C3–C4 108.9(3), C4–C3–B1 106.3(3).

These ¹¹B and ¹⁹F NMR parameters are both typical for the presence of a strongly Lewis acidic trigonal-planar R-B(C₆F₅)₂ structure.¹² The mesityl substituents at phosphorus (³¹P NMR: δ –16.2) are diastereotopic. In addition there is hindered rotation around the P–C(Mes) vectors at low temperature. Therefore, the ¹H NMR spectrum at 213 K shows a total of six mesityl methyl signals and four arene CH resonances. The ¹H NMR signals of the hydrogen atoms at the C(sp³)–C(sp³) bridge occur at δ 4.62 (2-H) and 2.16 (3-H), and the bridgehead ¹H NMR signals of the tricyclic P/B FLP framework were located at δ 4.33 and 4.29, respectively (for further details see the Supporting Information).

Reactions of Compound 8 with Phenylacetylene and with Dihydrogen. Compound 8 is a very reactive FLP, as anticipated. It undergoes a variety of typical FLP reactions under mild conditions with high reaction rates. For these reactions the FLP 8 was usually not isolated prior to use but was generated in situ by reacting the phosphane 7 with a stoichiometric quantity of $HB(C_6F_5)_{2^2}$ and then we used these freshly prepared solutions for the subsequent FLP reactions.

Many frustrated Lewis pairs react with the C-H bonds of terminal alkynes,¹³ and so does compound 8. Treatment of compound 8 with phenylacetylene (room temperature, dichloromethane, overnight) gave the zwitterionic phosphonium/alkynylborate product 9 in good yield (see Scheme 3). It shows a typical ¹¹B NMR signal (δ –17.6) of a tetravalent borate and a ³¹P NMR doublet of the [P]-H phosphonium unit at δ 1.6 (¹ $J_{PH} \approx$ 490 Hz, corresponding ¹H NMR doublet at δ 8.05). Both the phosphonium and the borate section are prochiral, and in addition, there is hindered rotation around both pairs of P-C(aryl) and $B-C_6F_5$ vectors. Consequently, we have observed six ¹H NMR methyl signals of the $-P(H)Mes_2$ unit and five (two overlapping) ¹⁹F NMR C₆F₅ signals of the $-B(alkynyl)(C_6F_5)_2$ substituent in compound 9. The ¹H NMR signals of the C1–C4 core are found at δ 4.61/ 4.52 (1-H, 4-H), 3.99 (2-H), and 2.72 (3-H); the last signal features a characteristically large ${}^{3}J_{PH} = 35.2$ Hz coupling constant.

Scheme 3. Reaction of the FLP 8 with Phenylacetylene and with Dihydrogen



The structural assignment of compound 9 was confirmed by its X-ray crystal structure analysis. The dihedral angle of the P1-C2-C3-B1 unit amounts to $\theta = -86.9(3)^{\circ}$. The $\sum P1^{CCC}$ value (sum of angles at the phosphonium phosphorus atom P1) amounts to 344.3°. The boron atom has the linear phenylacetylide substituent attached to it (for details of the structural characterization of compound 9, including the depicted molecular structure, see the Supporting Information).

We carried out a competition experiment of the phenylacetylene C-H activation reaction between the parent interacting P/B FLP 1 and the new open, noninteracting P/B FLP 8. It turned out that the system 8 is much more reactive toward the C-H acidic terminal acetylene. It reacts >20 times faster than the system 1 (conventionally estimated, for details see the Supporting Information).

The FLP 8 activates dihydrogen.^{3,14} The in situ generated open, noninteracting P/B frustrated Lewis pair reacts rapidly with H_2 under nearly ambient conditions (1.5 bar, room temperature) to give the dihydrogen splitting product 10.

On a preparative scale we stirred the reaction mixture for 2 h and isolated the product of heterolytic H₂ cleavage as a white solid in 77% yield. The X-ray crystal structure analysis (see Figure 2) shows the typical dibenzobicyclo[2.2.2]octadiene framework with the newly generated P(H)Mes₂ and BH- $(C_6F_5)_2$ phosphonium cation/borate anion units attached $(\theta(P1-C2-C3-B1) = -98.2(1)^\circ)$. The [P]-H vector is directed inside toward the boron atom, whereas the [B]-H vector is pointing upward almost normal to the [P]-H unit. We note that a mesityl ring at phosphorus and a C_6F_5 ring at boron are almost oriented parallel to each other.

In solution the hydrogen splitting product **10** shows a ¹¹B NMR hydridoborate [B]–H doublet at δ –20.3 (¹J_{BH} \approx 90 Hz) and a corresponding ³¹P NMR phosphonium signal at δ –6.5 with a typical large ¹J_{PH} \approx 480 Hz coupling constant (¹H NMR [P]–H signal at δ 6.50). The 1-H/4-H bridgehead ¹H NMR signals of compound **10** occur at δ 4.34 and 4.47, respectively, and their neighboring 2-H and 3-H resonances appear at δ 3.65 and δ 1.78, respectively. The mesityl groups at the phosphonium moiety are diastereotopic, and they show hindered rotation around the P–C(aryl) vectors at room temperature. Consequently, we have observed a total of six mesityl methyl ¹H/¹³C NMR resonances.

We have carried out the dihydrogen splitting reaction with dideuterium and obtained the respective [P]D/[B]D compound **10**-D₂. The corresponding phosphonium and hydridoborate ¹H NMR resonances are missing in the ¹H NMR spectrum of compound **10**-D₂, but we observe the respective



Figure 2. View of the dihydrogen splitting product **10** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): P1–C2 1.833(2), C1–C2 1.573(2), C2–C3 1.575(2), C3–C4 1.574(2), C3–B1 1.643(2); C1–C2–P1 115.1(1), C1–C2–C3 110.8(1), C2–C3–C4 106.5(1), C4–C3–B1 114.9(1).

signals in the ²H NMR spectrum as a broad [P]-D doublet (δ 6.5; ¹*J*_{PD} = 72.0 Hz) and a broad unstructured [B]-D signal at ca. δ 2.0. The ³¹P NMR spectrum of compound **10**-D₂ shows a 1:1:1 intensity triplet as expected (the ²H NMR spectra are depicted in the Supporting Information section).

We determined the relative rate of the dihydrogen splitting reaction between the pairs 1 and 8. From a competition experiment we determined that 8 actives H₂ under these conditions only marginally faster that the reference compound $(k_{\rm rel}$ at 263 K is *ca.* 2–3). This is surprising at first sight that the open nonbridged FLP 8 is about equal in H₂-splitting activity as the closed interacting FLP 1, which needs to open first in a preequilibrium step in order to be prepared to react with the dihydrogen molecule at all. In a separate experiment we assured that the hydrogen transfer reaction between the 2/8 and 1/10 pairs was much slower than the respective dihydrogen splitting reactions (for details including the depicted NMR spectra see the Supporting Information).

We note a principal difference in the behavior of the FLPs 1 and 8 from the competition experiments between the terminal acetylene and the dihydrogen splitting reaction. It seems that the phosphane in the FLP 8 just serves as an independent base in the deprotonation reaction of phenylacetylene with a subsequent separate addition step of the resulting alkynyl anion to the pendent borane Lewis acid. This makes the reaction of the FLP 8 with the terminal alkyne quite fast. In contrast, the H₂ splitting reaction of either of the frustrated Lewis pairs requires a cooperative action of the phosphane Lewis base and borane Lewis acid protagonists. A close inspection of the DFT calculated transition state geometry of the $1 + H_2$ reaction (1-TS in Scheme 1) had shown a P-C-C-B dihedral angle of the FLP backbone of -54.0°, which is actually not far away from that of the open gauche-like intermediate (1-open: 54.4°).¹⁵ In contrast, the P-C-C-B angle in the open, nonbridged FLP 8 is found (by X-ray diffraction) at -106° (see above), which is probably far away

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from an ideal situation for the cooperative H–H splitting reaction. Therefore, it seems that the system 8 pays a price for its increased separate Lewis acid and Lewis base reactivity in the H_2 -splitting situation where their cooperative action is apparently essential. We note that the degree of "frustration" is apparently not the sole decisive parameter in cooperative frustrated Lewis pair reactions; geometric and conformational features are at least of equal importance.

Other Typical FLP Reactions of the Noninteracting P/ **B** Pair 8. Many alkylboranes react with carbon monoxide by formation of acylboranes. This reaction has found frequent use for the preparation of ketones, aldehydes, or alcohols.¹⁶ In contrast, CO is not reduced by [B]-H boranes except when it is catalyzed.^{17,18} It has long been known that diborane B_2H_6 just forms borane carbonyl (H₃B-CO) on exposure to CO at high temperature and pressure. We had recently shown that even Piers' borane $HB(C_6F_5)_2$ shows this specific reaction pathway: it forms Piers' borane carbonyl $(C_6F_5)_2B(H)-CO_1^{-1}$ a compound that we had characterized by X-ray diffraction.¹⁹ However, CO is reduced to the formylborane stage by $HB(C_6F_5)_2$ at a variety of vicinal P/B FLP templates. We could show that by involvement of the FLP framework the thermodynamic restriction of the $(C_6F_5)_2B(H)$ -CO to formylborane conversion could be overcome, and we have isolated a number of FLP- η^2 -formylboranes.^{8,20} Compound **8** is no exception. Treatment of the FLP $8/HB(C_6F_5)_2$ mixture with CO (1.5 bar) at room temperature overnight gave the η^2 formylborane P/B FLP adduct 11, which we isolated as a white solid in 67% yield. We assume that the $(C_6F_5)_2B(H)$ -CO adduct is added to the P/B FLP 8 across the C \equiv O π system. The resulting activated carbonyl is then readily reduced by the adjacent in situ generated hydridoborate to directly give the product 11.

The X-ray crystal structure analysis of compound **11** shows the newly formed six-membered P/B-containing heterocycle trans-fused with the dibenzobicyclo[2.2.2]octadiene framework $(\theta(P1-C2-C3-B1) = -81.3(5)^\circ)$. At its distal position it contains the C5-O1 bond of the newly formed formyl group which is η^2 bonded to the B(C₆F₅)₂ moiety originating from the HB(C₆F₅)₂ reducing agent (see Figure 3).

In solution compound 11 features heteroatom NMR resonances at δ 30.6 (³¹P) and 7.5 (¹¹B). It shows the ¹⁹F NMR resonances of four pairwise diastereotopic C₆F₅ substituents at the pair of boron atoms, giving rise to four *p*-C₆F₅ signals and (at 213 K) a total of eight *o*-C₆F₅ resonances. Two *o*-C₆F₅ resonances show through-space coupling at 213 K (through-space coupling constant ^{TS}J_{FF} \approx 144 Hz; for details see the Supporting Information²¹). The ¹H NMR spectrum of compound 11 shows the formyl signal at δ 5.01 (d, ²J_{PH} = 12.7 Hz), and the ¹³C NMR spectrum shows this signal at δ 60.2 (¹J_{PC} = 60.7 Hz). The pair of diastereotopic mesityl groups at phosphorus shows hindered rotation around both P–C(aryl) vectors; consequently, we observed six mesityl methyl ¹H NMR signals at 299 K (for further details see the Supporting Information)

Some $(\eta^2$ -formylborane)FLP compounds showed a high reactivity toward H₂,^{8,20} and so does compound 11. Exposure of the η^2 -formylborane FLP adduct 11 to H₂ at 20 bar for 48 h at room temperature resulted in a clean reduction of the CO derived –CHO group to methylene. We isolated the product 13 (see Scheme 4) in 67% yield. We assume that facile reversible opening of the O–B1 linkage in 11 generates a reactive O/B frustrated Lewis pair that splits dihydrogen under



Figure 3. Projection of the molecular structure of the $(\eta^2 - \text{formylborane})$ FLP compound 11 (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): C5–O1 1.482(8), O1–B1 1.637(8), C5–B2 1.603(10), P1–C5 1.839(7), B2–O1 1.587(8), P1–C2 1.840(6), C1–C2 1.567(9), C3–B1 1.614(10); C5–B2–O1 55.4(4), B2–C5–O1 61.8(4), B2–O1–C5 62.9(4), C5–P1–C2 97.1(3), O1–B1–C3 100.7(5), P1–C2–C3–B1 –81.3(5).

Scheme 4. Formylborane Chemistry at the FLP 8 Template



the applied conditions to give the intermediate **12**. This contains an oxonium moiety and a neighboring hydridoborate nucleophile, and consequently, hydride attack at the adjacent carbon atom results in opening of the activated three-membered heterocycle to eventually yield the observed product **13** (see Scheme 4).

The X-ray crystal structure analysis of compound 13 confirmed the formation of the seven-membered heterocycle annulated with the "semi-triptycene" framework. It contains the trans-fused phosphonium and borate moieties ($\theta(P1-C2-C3-B1) = 91.6(2)^{\circ}$). The newly formed $-CH_2$ - group is found bridging between the phosphorus atom P1 and the boron atom B2. The former CO oxygen atom is attached to the pair of B1/B2 atoms and it is found to be protonated (see Figure 4).

The newly formed $[P]-CH_2-[B]$ methylene group shows up as a tight AB pattern in the ¹H NMR spectrum at δ 3.24 and a ¹³C NMR feature at δ 38.0. The corresponding [B]-OH-[B] ¹H NMR resonance occurs at δ 5.47 as a doublet with a



Figure 4. Molecular structure of compound **13** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): P1–C5 1.810(2), C5–B2 1.635(4), B2–O1 1.550(3), O1–B1 1.599(3), B1–C3 1.634(3), C2–C3 1.572(3), C2–P1 1.855(2); P1–C5–B2 119.4(2), B2–O1–B1 130.3(2), C5–B2–O1 106.4(2), O1–B1–C3 107.0(2), C2–P1–C5 104.4(1), P1–C5–B2–O1 54.3(2), C5–B2–O1–B1 45.8(3), B1–C3–C2–P1 91.6(2).

⁴*J*_{PH} = 13.3 Hz coupling constant. Again, rotation of the diastereotopic pair of the bulky mesityl groups around their P– C(aryl) σ bonds is hindered, leading to the observation of six methyl ¹H NMR (as well as six ¹³C NMR) signals at 299 K, and we have monitored the ¹⁹F NMR signals of four separate C₆F₅ groups of the pair of B(C₆F₅)₂ moieties; two of the o-C₆F₅ resonances show through-space coupling at 299 K (^{TS}*J*_{FF} ≈ 112 Hz; for details see the Supporting Information).

We had shown that a variety of vicinal P/B FLPs undergo metal-reminiscent 1,1-addition reactions with typical organic ligands such as CO,²² isonitriles,²³ and NO^{24,25} to give fivemembered heterocyclic products. In these reactions the boron atom serves as a typical Lewis acceptor to the lone pair and the phosphorus donor is able to mimic a back-bonding reactivity to the π^* orbital of these reagents. Compound 8 reacts accordingly with nitric oxide (NO). The in situ generated P/ B FLP 8 reacts rapidly in a dichloromethane/n-pentane mixture at room temperature with NO (1.5 bar, 1 h) to give a blue precipitate of the P/B FLPNO[•] nitroxide radical.²⁴ The paramagnetic compound was characterized by C,H,N elemental analysis and by X-ray diffraction (see Figure 5). The X-ray crystal structure analysis shows the five-membered heterocycle that was formed by N₁N addition of the P/B pair of 8 to nitric oxide. The NO attachment to the Lewis pair is rather symmetrical (angles P1-N1-O1 = $119.3(2)^{\circ}$, B1-N1-O1 = 125.0(3)°). The N1-O1 bond length is 1.288(3) Å. This is longer than the N–O distance in free nitric oxide $(1.15 \text{ Å})^{26}$ but still rather short, which indicates some significant delocalization of the oxygen and nitrogen in this persistent nitroxide radical.^{24,25} The nitrogen atom in the radical 14 has a typical planar coordination geometry ($\sum N1^{PBO} = 359.9^{\circ}$). Some FLPs add to $N_2O_2^{27}$ and others are easily oxidized. The

Some FLPs add to $N_2O_1^{2/2}$ and others are easily oxidized. The latter occurs upon treatment of the P/B FLP 8 with N_2O . We isolated the oxidation product 15 in good yield (see Scheme 5). See the Supporting Information for its characterization (including the X-ray crystal structure analysis).



Figure 5. Molecular structure of persistent P/B FLPNO[•] radical 14 (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): C2–P1 1.800(4), P1–N1 1.731(3), N1–B1 1.618(5), B1–C3 1.623(5), C2–C3 1.567(5); C2–P1–N1 90.3(2), P1–N1–B1 115.6(2), N1–B1–C3 96.7(3), P1–C2–C3–B1 –60.6(3).





Many FLPs add to heterocumulenes.²⁸ The reactions with *N*-sulfinylaniline are special in that different types of products are sometimes observed. We had found the cationic metal FLP based PhN=S=O addition products **16** and **17**,²⁹ and Stephan et al. discovered the 1,3-P/B FLP addition product **18** and its chemistry.³⁰ We reacted the P/B FLP **8** with sulfinylaniline in a 1:1 molar ratio at room temperature overnight and isolated the addition product **19** as a yellow solid in 64% yield (see Scheme 6). It shows ¹H NMR resonances of the four saturated CH bonds of the framework at δ 4.64/4.80 (bridgehead portions 1-H, 4-H, with corresponding ¹³C NMR signals at δ 47.0 (C1) and 47.9 (C4), respectively), 4.60 (2-H; ¹³C δ 51.9), and 3.59 (dd, ³J_{PH} = 24.7 Hz, ³J_{HH} = 9.1 Hz, 3-H; ¹³C δ 37.1). Compound **19** features heteroatom NMR





resonances at δ 3.0 (¹¹B) and 55.0 (³¹P) and two equalintensity sets of ¹⁹F NMR signals of the diastereotopic C₆F₅ substituents at boron.

Compound 19 was characterized by an X-ray crystal structure analysis (see Figure 6). It revealed that 1,3-addition



Figure 6. View of the molecular structure of compound **19** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): P1–N1 1.695(2), N1–S1 1.710(2), S1–O1 1.608(2), O1–B1 1.522(3), B1–C3 1.647(4), C2–C3 1.579(3), C2–P1 1.859(2); C2–P1–N1 108.5(1), C3–B1–O1 110.6(2), P1–C2–C3–B1 –88.8(2).

of the P/B pair to the heterocumulene had taken place, forming a seven-membered heterocycle. The phosphorus atom was attached to the nitrogen atom of the reagent and the boron atom ended up bonded to oxygen. This resulted in a bent geometry at both oxygen (angle B1–O1–S1 = 114.0(2)°) and also sulfur (angle O1–S1–N1 = 103.9(1)°). The boron and phosphorus atoms in compound **19** both show pseudotetrahedral coordination geometries, and the nitrogen atom N1 is planar tricoordinate ($\sum N1^{PSC} = 356.8^{\circ}$).

1,4-P/B FLP Addition to 1,2-Dicarbonyl Compounds. P/B FLPs often add to carbonyl compounds. This usually gives the 1,2-addition products, which feature a new pair of B-O and P-C bonds.³¹ P/B FLPs may also undergo 1,2-carbonyl addition reactions to conjugated enones and ynones, but in many cases conjugated 1,4-addition prevails.^{32,33} Especially, a number of vicinal P/B FLPs were shown to yield the respective eight-membered heterocyclic product from such 1,4-addition reactions. This posed a question of the outcome of the exposure of the reactive vicinal P/B FLP 8 to 1,2-dicarbonyl compounds. In principle, one might envisage a clear case of 1,2addition to one activated C=O group. However, a DFT calculation³⁴ revealed that the 1,4-addition might be much more favorable. The calculation was carried out on the reaction of the P/B FLP 8 with the 1,2-diketone 20 by using two density functional methods: i.e., optimization by the PBEh-3c composite approach followed by PW6B95-D3/def2-TZVP single-point energies. It showed an exergonic formation of the 1,2-addition product 22, but the formation of the 1,4addition product 21 was ca. 10-12 kcal mol⁻¹ more favorable (see Scheme 7 and the Supporting Information). We performed this reaction experimentally by reacting the P/B

Scheme 7. Reactions of the P/B FLP 8 with 1,2-Diketones



FLP 8 with the acenaphthene quinone 20 in a 1:1 molar ratio in dichloromethane solution at room temperature (overnight). Workup then gave the 1,4-addition product 21 as a yellow solid in 58% yield.

Compound **21** was characterized by C,H elemental analysis, spectroscopy, and X-ray diffraction. The X-ray crystal structure analysis (see Figure 7) shows the formation of the eight-



Figure 7. View of the 1,4-dicarbonyl addition product 21 (thermal ellipsoids are shown with 50% probability). Selected bond lengths (Å) and angles (deg): P1–O1 1.590(1), O1–C71 1.400(2), C71–C81 1.357(3), C81–O2 1.344(2), O2–B1 1.526(2), B1–C3 1.647(3), C2–C3 1.565(3), C2–P1 1.831(2); C2–P1–O1 109.2(1), P1–O1–C71 131.2(1), O1–C71–C81 128.6(2), C71–C81–O2 128.6(2), C81–O2–B1 118.7(1), O2–B1–C3 109.7(2), P1–C2–C3–B1 –91.4(2).

membered heterocycle by formation of a new pair of B–O and P–O σ bonds. There is now a C==C double bond between the former carbonyl carbon atoms of the introduced reagent **20**, now completing the acenaphthene π system inside the addition product.

In CD₂Cl₂ solution compound **21** features a phosphonium ³¹P NMR resonance at δ 86.8 and a broad ¹¹B NMR signal at δ

1.4. It shows the ¹⁹F NMR signals of a pair of diastereotopic C_6F_5 substituents at boron. We monitored the ¹H/¹³C NMR signals of a pair of diastereotopic mesityl groups at phosphorus, which show hindered rotation around both the P–C(mesityl) vectors at 299 K (giving rise to each six CH₃ ¹H NMR and ¹³C NMR resonances at room temperature). The former pair of carbonyl carbon atoms now has formed the acenaphthene C== C double bond. We have assigned to them the ¹³C NMR resonances at δ 149.2 (³J_{PC} = 5.3 Hz) and 131.6 (²J_{PC} = 12.4 Hz), respectively.

The reaction of the P/B FLP **8** with benzil takes a similar course. Workup of the reaction mixture after stirring at room temperature overnight gave the 1,4-dicarbonyl addition product **23**, which we isolated in 83% yield. The X-ray crystal structure analysis (see Figure 8) of compound **23** shows the presence of



Figure 8. Molecular structure of the 1,4-addition product **23** of the vicinal P/B FLP **8** to benzil (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): P1–O1 1.597(2), O1–C71 1.448(4), C71–C72 1.342(5), C72–O2 1.362(4), O2–B1 1.526(5), B1–C3 1.658(6), C2–C3 1.565(5), C2–P1 1.851(4); C2–P1–O1 106.6(1), P1–O1–C71 121.9(2), O1–C71–C72 117.6(3), C71–C72–O2 120.7(3), C72–O2–B1 122.4(3), O2–B1–C3 105.8(3), P1–C2–C3–B1 88.9(3).

the [P]-O-C(Ph)=C(Ph)-O-[B] section of the newly formed eight-membered ring and, thus, confirms that this reaction of the P/B FLP with the 1,2-dicarbonyl reagent also occurred by 1,4-addition.

In solution compound **23** features the ¹³C NMR signals of the newly formed carbon–carbon linkage at δ 148.8 ("BOC", ³ $J_{PC} = 5.3$ Hz) and 136.1 ("POC", ² $J_{PC} = 13.5$ Hz). The heteroatom NMR signals of compound **23** occur at δ 0.6 (¹¹B) and 85.3 (³¹P), respectively, and compound **23** shows a total of ten well-separated ¹⁹F NMR resonances of the diastereotopic pair of C₆F₅ substituents at boron.

Since the reactivity of the new intramolecular nonbridged vicinal P/B FLP 8 resembled the reactivity of intermolecular FLP systems, we treated the acenaphthene quinone reagent **20** with the intermolecular ${}^{t}Bu_{3}P/B(C_{6}F_{5})_{3}$ FLP³⁵ under analogous conditions (dichloromethane solution, room temperature, overnight). We observed the analogous 1,4-addition reaction to this 1,2-diketone. Workup gave the product **24** in 85% yield as an orange solid (see Scheme 8). In this case the DFT

Scheme 8. 1,4-Addition of the ${}^{t}Bu_{3}P/B(C_{6}F_{5})_{3}$ FLP with a 1,2-Diketone



calculation revealed that the formation of the observed 1,4-addition product **24** was favored over the (not experimentally observed) 1,2-addition product by ca. 24 kcal mol^{-1} .

The X-ray crystal structure analysis confirmed the 1,4-P/B addition with formation of the completed acenaphthene π system with vicinal $(C_6F_5)_3B-O-$ and ${}^tBu_3P-O-$ substituents at the C=C double bond at the five-membered subunit (see Figure 9). Both of these substituents are strongly bent at their oxygen atoms, and the P–O and B–O vectors are oriented toward opposite faces of the acenaphthene framework.



Figure 9. Molecular structure of compound **24**. Selected bond lengths (Å) and angles (deg): P1–O1 1.589(2), O1–C1 1.408(3), C1–C2 1.367(4), C2–O2 1.346(3), O2–B1 1.517(3); P1–O1–C1 136.6(2), C2–O2–B1 123.2(2), P1–O1···O2–B1 124.3.

In solution compound **24** shows the typical NMR features of the acenaphthene framework with the C==C unit inside the five-membered ring giving rise to ¹³C NMR signals at δ 149.7 ("BOC", ³ J_{PC} = 4.1 Hz) and 132.7 ("POC", ² J_{PC} = 18.5 Hz): i.e., NMR features similar to those observed for the related compounds **21** and **23** (see above). Compound **24** shows a ¹¹B NMR signal at δ –2.0 in the typical borate range and a phosphonium ³¹P NMR resonance at δ 110.3. The ¹⁹F NMR pattern is rather complicated, apparently showing three different sets of C₆F₅ signals due to a probably frozen propeller geometry (for details see the Supporting Information).

CONCLUSIONS

By exploring the new open P/B FLP 8 we found a new FLP reaction motif, namely the 1,4-P/B addition to 1,2-dicarbonyl compounds.³⁶ Our DFT study has revealed a thermodynamic preference of 12-14 kcal mol⁻¹ of the 1,4- over the conventional 1,2-addition for our first example, which makes the 1,4-product favored by far even under equilibrium conditions. The preferred formation of the 1,4-addition

products (21, 23, 24) may indicate a special reactivity of the FLP 8, making this an intramolecular P/B FLP with a reactivity pattern resembling an intermolecular case.

Many intermolecular FLPs show high reactivities in smallmolecule activation.³⁵ They circumvent the kinetic trap of termolecularity (i.e., the necessity of three reagents coming together to allow for a reaction to take place between them), e.g. in the H₂ splitting reaction, by forming an "encounter complex" in a preequilibrium step from which the actual cooperative H–H cleavage can take place.³⁷ Computational studies have merged to ascribe the intermolecular Lewis acid/ base interaction based on a sum of van der Waals contacts in a dynamic situation,^{38,39} which leads to a transition state of the H₂ splitting reaction with a side-on arrangement of the H–H molecule at the boron atom with a nearly linear arrangement of the H–H–LB vector.^{15,37}

Intramolecular FLPs do not have the termolecularity problem, since both the Lewis acid and the Lewis base are intramolecularly connected. The H_2 splitting transition state, nevertheless, has computationally been found to be quite similar to the intermolecular case, namely showing a side-on arrangement of the H–H vector to the borane and a close to linear orientation of the H–H–Lewis base unit (see Scheme 1 for an example).⁴⁰

Many intramolecular FLPs, however, may pay a price by featuring an internal interaction between the core atoms of the Lewis pair along the connecting organic framework. This especially holds for the many vicinal P/B FLPs that have been reported so far. In order to function as active frustrated Lewis pairs they must dissociate, breaking the P···B interaction, in a preequilibrium step, before they can undergo any of their typical cooperative small-molecule reactions. Fortunately, the LA–LB dissociation of many intramolecular P/B FLPs is thermodynamically mildly endergonic (e.g., 7–8 kcal mol⁻¹ for our "parent" ethylene-bridged P/B FLP 1,⁷ see above) and the activation barriers of equilibration are low;⁴¹ nevertheless these equilibrium parameters contribute to the overall situation of any subsequent FLP reaction.

The development of open, nonbridged intramolecular FLPs might, therefore, be of importance. However, we found out that the example described here of the trans-vicinal P/B FLP 8 at the symmetrical "semi-triptycene" framework shows a similar activity in the H_2 splitting reaction as the interacting FLP 1. Compound 8 does surprisingly not profit much from having a kinetic advantage over 1 in featuring an open-nonbridged structure. This probably means that the intrinsic reactivity of the high-lying 1-open isomer must be much higher than that of the open ground state structure of 8, since it must kinetically compensate for the unfavorable 1-closed \rightleftharpoons 1-open equilibrium situation. It is likely that this is due to the much higher flexibility of the 1-open isomer over the rather rigid system 8, resulting in an effective lowering of the decisive structurally rather demanding FLP-H₂ splitting transition state. Consequently, we must conclude that frustration (i.e., the absence of an effective Lewis acid/Lewis base interaction) alone is not an exclusive criterion for FLP reactivity. It seems that geometric factors and conformational flexibility to reach the decisive transition state geometries is also of great importance. In our special case this conformational feature seems to largely compensate for the kinetic disadvantage that the 1-closed system has over our new open, nonbridged FLP 8 in the heterolytic H₂ splitting reaction, so that they both show similar overall reactivities toward dihydrogen.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00819.

Experimental, analytical, and DFT calculation details (PDF)

Accession Codes

CCDC 1576800–1576811 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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