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Phospha-Claisen Type Reactions at Frustrated Lewis Pair Frameworks

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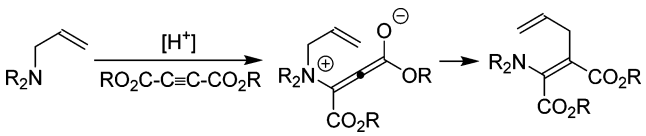
Supporting Information

ABSTRACT: The C_4-bridged unsaturated phosphane/borane frustrated Lewis pairs (P/B FLPs) **4** undergo borane induced phosphane addition to a variety of acetylenic esters or ketones to generate heterocyclic 10-membered intermediates that contain pairs of allyl phosphonium/allenic enolate functionalities. These subsequently undergo phospha-Claisen type rearrangement reactions to give the respective substituted phosphanyl pentadiene products. In two exceptional cases subsequent reactions leading to anomalous phospha-Claisen products were found. One example involved cyclopropane ring formation, and the other carbon−carbon bond activation. Potential mechanistic schemes leading to these products are discussed. Essential examples were characterized by X-ray diffraction.

INTRODUCTION

The aza-Claisen Reaction. Vedejs and Gingras described a sequence of acid catalyzed allylamine addition to acetylene dicarboxylate followed by a formal [3,3]sigmatropic rearrangement and used this "aza-Claisen" type rearrangement for the formation of various amino-functionalized pentadiene frameworks (Scheme 1).[1,2] There had been reports that simple

Scheme 1

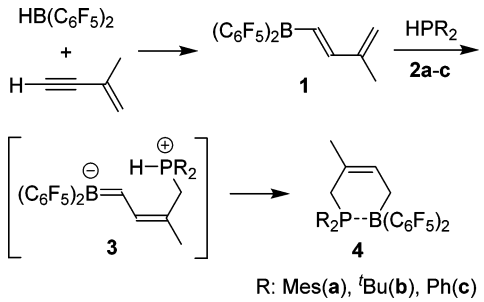


phosphanes such as, e.g., Ph_3P readily added to acetylene dicarboxylate.[3−5] This posed the question whether a phosphorus analogue of Vedejs' reaction sequence, a "phospha-Claisen" type reaction could be achieved by reacting a suitably substituted allylphosphane with this and related acetylenes under suitable reaction conditions to eventually yield the respective phosphanyl-pentadiene systems. In this report, we will describe that the phospha-Claisen reaction scheme can be realized within a suitably devised phosphane/borane frustrated Lewis pair framework,[6] but some of the systems investigated furnished some surprising results.

RESULTS AND DISCUSSION

The Phospha-Claisen Reaction. We had recently prepared a small series of unsaturated C_4-bridged phosphane/borane frustrated Lewis pairs **4a−c** (P/B FLPs) by treatment of the dienyl borane **1** with the respective secondary phosphanes **2a−c** (see Scheme 2).[7] The reaction probably proceeds by means of a reactive conjugated borata-alkene[8] intermediate **3** followed by proton transfer.

Scheme 2



The P/B FLPs **4** contain three interlocked functionalities, namely an allylborane, an allylphosphane and a phosphane/borane Lewis pair.[9] We had previously found a few reactions (e.g., with aldehydes) which made use of a combination of allylboration/FLP addition reactions.[10] We have now found that the systems **4** react with acetylenic esters and ketones by using their allylphosphane functional group in conjuction with the adjacent boron Lewis acid functionality.

We first reacted the Mes_2P containing FLP **4a** with the acetylene carboxylic ester **5a**. The reaction went to completion in dichloromethane solution at r.t. within 5 h. Workup eventually gave the product **8a** (see Scheme 3 and Table 1) as a yellow solid in 90% yield. It was characterized by C,H elemental analysis, by spectroscopy and by X-ray diffraction.

The X-ray crystal structure analysis showed that the alkyne reagent **5a** had been added to the FLP **4a** and the product was formed by means of phospha-Claisen type rearrangement pathway (see Figure 1). We assume activation of the ester by carbonyl coordination to the strong boron Lewis acid and subsequent formation of an allenic boron enolate intermediate

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Scheme 3

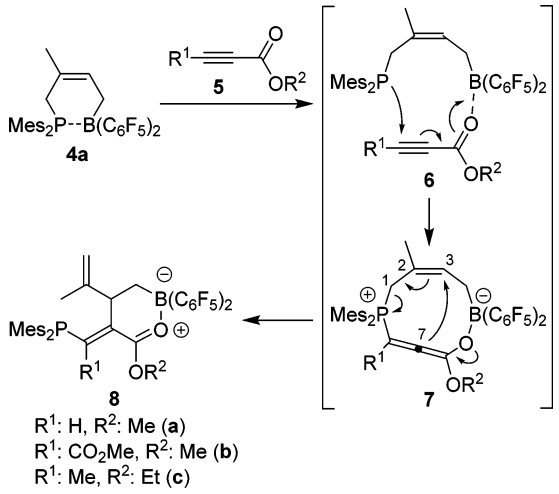


Table 1. Selected Structural Parameters of the "Phospha-Claisen Products" 8a and 8b[a]

	8a	8b
R^1/R^2	H/Me	CO_2Me/Me
P1–C6	1.828(3)	1.819(3)
C6–C7	1.340(4)	1.364(4)
C7–C8	1.461(4)	1.469(4)
C8–O1	1.255(4)	1.257(3)
C8–O2	1.310(4)	1.300(3)
B1–O1	1.585(4)	1.563(3)
B1–C4	1.604(5)	1.596(4)
O1–B1–C4	106.0(2)	104.7(2)
C8–C7–C6	118.2(3)	119.2(2)
P1–C6–C7-C8	−173.7(2)	175.5(2)
C6–C7–C8-O1	−170.2(3)	162.4(2)
ΣP^{CCC}	305.8	326.2

[a]Bond lengths in Å; angles in deg.

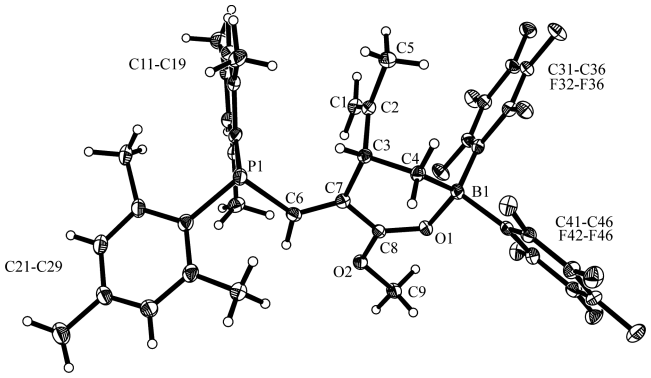


Figure 1. Projection of the molecular structure of the "phospha-Claisen product" **8a** (thermal ellipsoids are shown at the 30% probability level).

(**7a**) by means of nucleophilic phosphane addition to the Michael-position of the acetylenic ester, followed by C7–C3 bond formation across the ring and cleavage of the C1–P linkage (see Scheme 3).

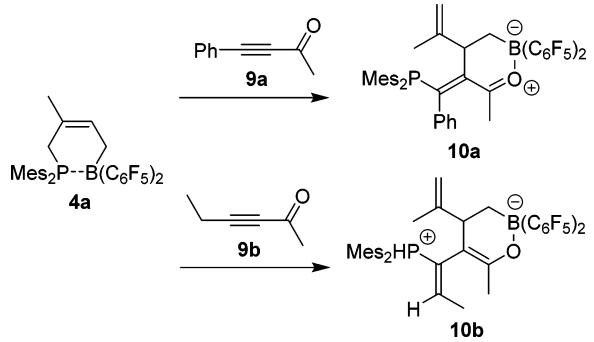
Consequently, the structure of compound **8a** (see Figure 1) features the newly formed P1–C6 bond as well as the new C7–C3 carbon–carbon σ-bond. Carbon atom C3 bears the –CMe(=CH_2) substituent that was liberated from the phosphorus center in the course of the formal phospha-Claisen sequence. The carbonyl oxygen atom (O1) of the resulting α,β-unsaturated ester unit is found bonded to boron (B1) as expected (see Table 1 and the Supporting Information for additional details).

Compound **8a** shows heteroatom NMR signals at δ −28.9 (^{31}P) and δ 3.4 (^{11}B), respectively. It shows ^{1}H/^{13}C NMR features of the newly introduced C7=C6(H) carbon–carbon double bond at δ 128.9 ($^2J_{PC}$ = 19.1 Hz, C7) and δ 158.9 ($^1J_{PC}$ = 20.5 Hz, C6) [^{1}H: δ 8.23 ($^2J_{PH}$ = 7.1 Hz, 6-H)], respectively. The –CMe(=CH_2) substituent shows ^{1}H NMR resonances at δ 4.40, 4.35 (=CH_2) and δ 1.24 (CH_3), respectively.

The reaction of the FLP **4a** with dimethylacetylene dicarboxylate **5b** takes an analogous course. Workup of the pentane reaction mixture after 1 h at r.t. gave the product **8b** in 83% yield. It was also characterized by X-ray diffraction (for details, see the Supporting Information). The product **8c** was formed analogously from **4a** and the 2-butynoate ester **5c**. Both products show typical NMR data [^{31}P: δ −28.2 (**8b**), δ −11.0 (**8c**); ^{11}B: δ 4.0 (**8b**), δ 2.8 (**8c**)], indicating the presence of a free phosphane and ester coordination to the boron Lewis acid.

The FLP **4a** undergoes the analogous reactions with some ketones. Treatment of **4a** with the phenyl substituted acetylenic ketone **9a** gave the Michael-addition/phospha-Claisen rearrangement product **10a** (isolated in 90% yield, ^{31}P NMR: δ −4.7, ^{11}B: δ 2.0) (see Scheme 4). The conjugated hexynone

Scheme 4



reagent **9b** reacted in principle analogously with the P/B FLP **4a**. However, in this case the initial phospha-Claisen product undergoes a subsequent intramolecular deprotonation reaction by the phosphane base at the pendent ethyl substituent to eventually form the conjugated boron enolate system **10b** (see Scheme 4). The compound was isolated after a reaction time of 5 d at r.t. from the pentane reaction mixture as a yellow solid in 76% yield and characterized spectroscopically and by C,H-elemental analysis (for details of the characterization of the products **10a,b**, see the Supporting Information).

We assume that in all these cases a stepwise reaction pathway is followed which proceeds through a medium-sized cyclic allenic enolate intermediate of the type **7** (see Scheme 3).[11,12] However, in all these cases described above, we were not able to obtain any direct evidence of the actual formation of **7** or an analogous intermediate under our typical reaction conditions. This changed when we investigated the reaction of the related P/B FLP **4b** (featuring the more nucleophilic ^{t}Bu$_2$P Lewis base)[7] with the acetylenic ketone **9b**. The reaction was carried out in pentane (3 h) at room temperature. In this case the reaction stopped at the stage of the allenic boron enolate **11a**

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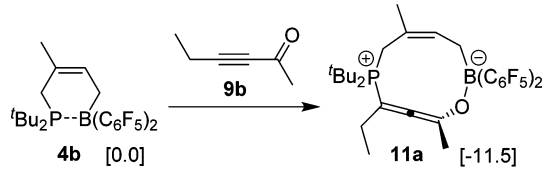
(see Scheme 5). It was isolated as a yellow solid in 81% yield and characterized by C,H-elemental analysis, by spectroscopy, and by X-ray diffraction.

Scheme 5



The X-ray crystal structure analysis (see Figure 2) shows the presence of a ten-membered heterocyclic ring. It has the

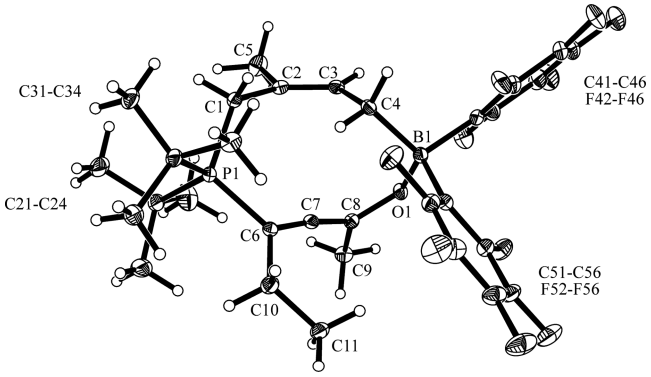


Figure 2. Molecular structure of compound **11a**. Thermal ellipsoids are shown at the 15% probability level. Selected bond lengths (Å) and angles (deg): P1−C1, 1.835(4); P1−C6, 1.813(4); B1−C4, 1.642(6); B1−O1, 1.494(5); C2−C3, 1.322(5); C6−C7, 1.305(5); C7−C8, 1.326(5); C1−P1−C6, 113.3(2); C4−B1−O1, 111.4(3); P1−C6−C7, 115.7(3); O1−C8−C7, 125.7(3).

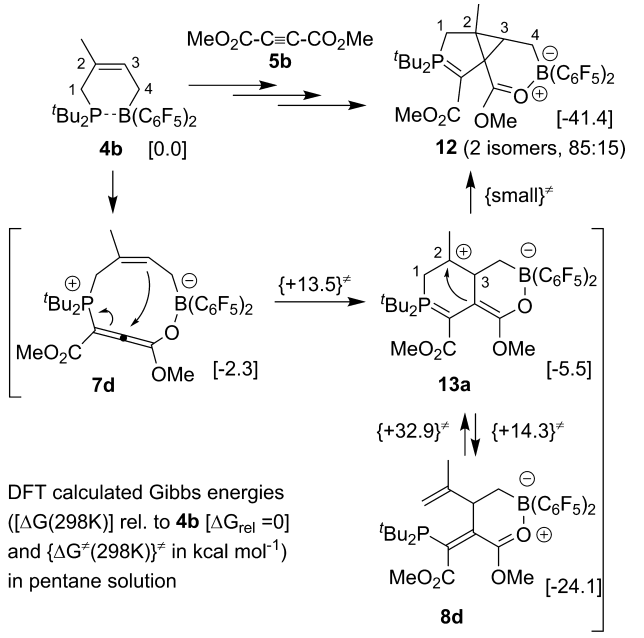
phosphonium type phosphorus atom bonded to the allene carbon atom C6. The allene unit is close to linear (C6−C7−C8 173.1(4)) and it has the planes of the substituents at its terminal carbon atoms C6 and C8 oriented close to normal (P1−C6−C10 vs O1−C8−C9 plane: 84.9°). The allenic enolate oxygen atom (O1) is bonded to boron (B1). The unsaturated C_4-chain is connecting boron and phosphorus. The C1−C2−C3-C4 unit is planar (with the methyl group at C2). It is strongly folded against the P-allenic-enolate-B unit (see Figure 2)

Compound **11a** shows typical allene ^{13}C NMR features[13] [δ 92.7 ($^1J_{PC}$ = 63.1 Hz, C6), δ 225.7 ($^2J_{PC}$ = 4.3 Hz, C7) and δ 135.3 ($^3J_{PC}$ = 12.9 Hz, C8)]. The ring =C3H ^{1}H NMR signal was located at δ 5.89. Compound **11a** shows heteronuclear magnetic resonance signals at δ 31.8 (^{31}P) and δ −1.1 (^{11}B). Due to the allene chirality we have observed the ^{1}H NMR signals of a pair of diastereotopic ^{t}Bu substituents at phosphorus and the ^{19}F NMR resonances of a pair of diastereotopic C_6F_5 substituents at boron (for further details, see the Supporting Information).

Anomalous Phospha-Claisen Reactions. So far, the reactions of our doubly allylic P/B FLPs (**4a**,**b**) with the acetylenic esters and ketones (**5**, **9**) were similar to Vedejs' allylamine derived aza-Claisen sequences,[1] although we found it amazing that such a reaction scheme can also be observed in the allylphosphane cases. However, two of our allylphosphane reactions with acetylenic esters or ketones had a markedly different outcome.

The first such example was encountered when we treated the ^{t}Bu$_2$P containing FLP **4b** with dimethylacetylene dicarboxylate **5b**. The FLP **4b** was stirred with one molar equivalent of the acetylene dicarboxylate **5b** in pentane solution for 3 h at room temperature. Workup gave compound **12** as a pale yellow solid as a 85:15 mixture of two stereoisomers in a combined yield of 85% (see Scheme 6). Single crystals suited for the X-ray crystal

Scheme 6



structure analysis were obtained at low temperature (−35 °C) from pentane/dichloromethane by the diffusion method. It revealed the formation of a heterotricyclic framework that contained a central cyclopropane ring, a borane coordinated ester in the annulated six-membered heterocycle and a phosphorus ylide moiety[14] in the five-membered heterocyclic fragment (Figure 3). Inside this remarkable structural array, the phosphorus atom has a pair of ^{t}Bu substituents bonded. It features a P1−C1 (1.828(2)Å) single bond and a much shorter P1═C6 (1.728(2)Å) bond of the ester stabilized P-ylide inside the five-membered ring. This ring is *cis*-fused with the central three-membered ring which bears the methyl substituent at the bridgehead carbon atom C2. In this product, the six-membered B−O containing heterocycle is also *cis* fused with the central cyclopropane unit and the C3−H and C2-CH_3 vectors are *trans* oriented. A molecular model inspection shows that the minor isomer might have these groups *cis* arranged at the C2−C3 linkage and consequently the six-membered heterocycle *trans* fused at the central cyclopropane ring (see the Supporting Information for NMR and DFT details).

The major compound monitored in solution shows NMR features that are consistent with the molecular structure of **12** found in the solid state. It features a ^{11}B NMR signal at δ 3.8 and two sets of *o*,*p*,*m*-^{19}F NMR resonances of the pair of diastereotopic C_6F_5 groups at boron with small $\Delta\delta^{19}F_{p,m}$ chemical shift differences typical of four-coordinate boron in such a situation. Compound **12** shows a ^{31}P NMR resonance at

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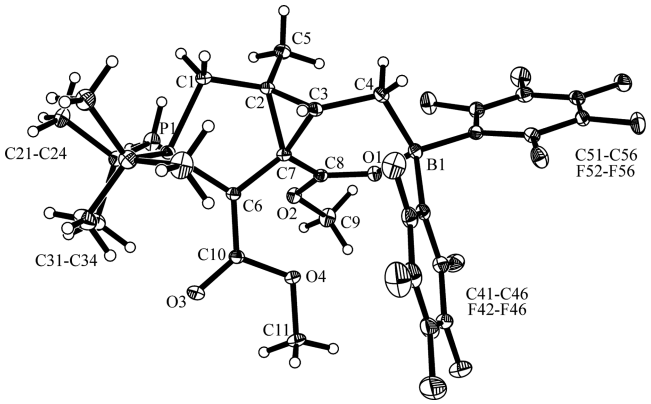


Figure 3. View of the molecular structure of compound **12**. Thermal ellipsoids are shown with 15% probability. Selected bond lengths (Å) and angles (deg): P1−C1, 1.828(2); P1−C6, 1.728(2); B1−C4, 1.595(3); B1−O1, 1.600(3); C8−O1, 1.252(3); C8−O2, 1.299(3); C1−P1−C6, 96.5(1); C4−B1−O1, 105.6(2); C2−C3−C7, 61.0(1); C3−C7−C2, 58.9(1); C7−C2−C3, 60.2(1).

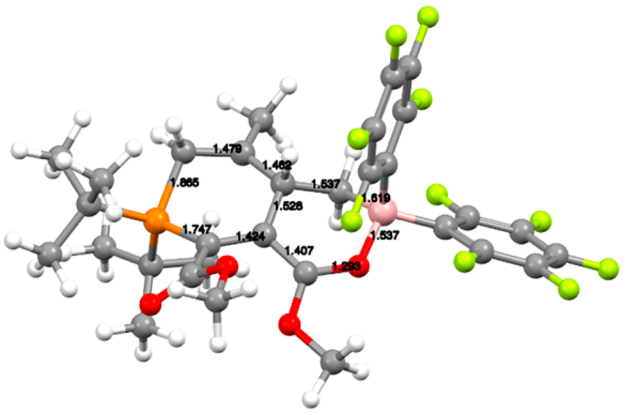


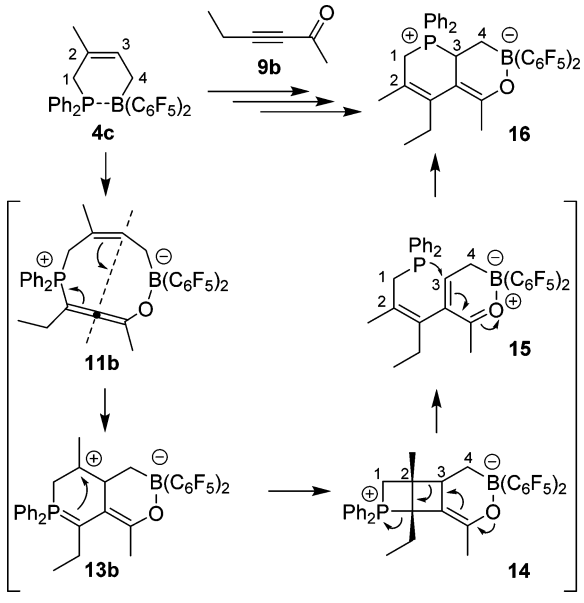
Figure 4. DFT calculated structure of the intermediate **13a**.

δ 80.1 which is a typical phosphorus ylide value.[15] It shows the $^{1}H/^{13}C$ NMR signals of the pair of ester groups. The [P]-CH_2− protons are diastereotopic and give rise to a typical AB pattern with an additional $^{2}J_{PH}$ coupling. The [P]=C(R)CO_2CH_3 ylide ^{13}C NMR signal is found at δ 48.4 ($^{1}J_{PC}$ = 113.0 Hz) and we found the ^{1}H NMR resonance of the single cyclopropane CH at δ 1.97. We could not positively identify the structure of the minor isomer of **12** from the NMR spectra of the mixture but note that it has very similar NMR data, e.g., δ 71.1 (^{31}P), and it shows a similar set of ^{19}F NMR signals of a pair of pentafluorophenyl substituents at boron. We assume that this is a stereoisomer of **12** (see the Supporting Information for some details).

The reaction pathway depicted in Scheme 6 was analyzed by DFT calculation. All calculations were performed with the TURBOMOLE 7.0 program.[16a] The structures were optimized without any geometry constraints using the TPSS functional[16a,b] and an atom-pairwise dispersion correction (D3).[16c,d] A flexible triple-ζ basis set (def2-TZVP)[16e] was used in all calculations. For the calculation of zero point vibrational energies and free enthalpy contributions, a rotor approximation was applied for vibrational modes with wave numbers below 100 cm^{-1}.[16f] Single point calculations were performed with the hybrid functional PW6B95(-D3).[16g] Free energies of solvation were obtained with the COSMO-RS model[16h,i] for 298 K using pentane as solvent. The calculation showed that the reaction of the B/P FLP **4b** with acetylene dicarboxylate **5b** to give the alleged 10-membered heterocyclic allenic boron enolate **7d** is exergonic (−2.3 kcal mol^{-1}, see Scheme 6). Subsequent formation of the phospha-Claisen product **8d** would also be strongly exergonic (−24.1 kcal mol^{-1} rel to **4b** + **5b**), but the DFT calculation did not locate any reasonable transition state for the direct **7d** to **8d** rearrangement on this hypersurface. However, it found that the **7d** to **13a** ring closure (with retaining of the P−C1 linkage) has a low barrier. The DFT calculated structure of the intermediate **13a** features a trigonal planar carbon center C2 with typically shortened C2−C1 and C2−C3 bond lengths (see Figure 4). The resulting intermediate **13a** could then easily rearrange to the phospha-Claisen product **8d** (which might actually also be considered as possible pathway for the other phospha-Claisen rearrangements described above), but in this special case reaction branching to give the tricyclic product **12** is by chance kinetically and thermodynamically favored. Unfortunately, we could not locate the transition state of the **13a** to **12** ring closure reaction with our single-reference DFT methods, but we obtained evidence that the barrier is below the **13a** to **8d** transition in this case (for details, see the Supporting Information).

This is not the only example of an anomalous course within the reaction manifold of the phospha-Claisen type chemistry. We found another related example, albeit with a different final outcome. In this case we reacted the PPh_2 derived P/B FLP **4c** with the hexynone reagent **9b**. The reaction of this FLP with the least nucleophilic phosphanyl group of the compounds **4** was slow at r.t. (checked in situ by NMR in C_6D_6). Therefore, we performed this reaction in toluene at elevated temperature (60 °C) for 3 d. Workup then gave a pale yellow solid of product **16**, which we isolated in 73% yield (see Scheme 7). Single crystals of compound **16** were obtained from dichloromethane/pentane at −35 °C by the diffusion method. The X-ray crystal structure analysis of compound **16** shows the unsaturated heteroatom containing bicyclo[4.4.0]decane derived framework. It features the phosphonium unit in one ring and the boron atom in the other. A conjugated dienolate unit is

Scheme 7



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part of both rings and its oxygen atom complements the tetracoordination of the boron atom B1 (see Figure 5).

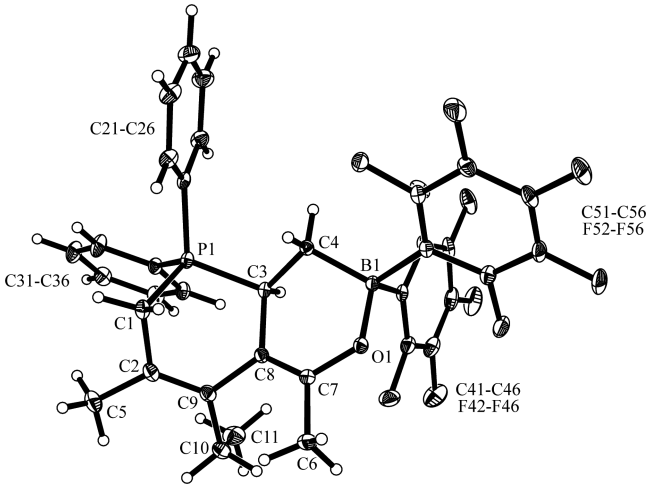

Figure 5. Molecular structure of compound **16**. Thermal ellipsoids are shown with 15% probability. Selected bond lengths (Å) and angles (deg): P1−C1, 1.800(3); P1−C3, 1.833(2); B1−C4, 1.623(4); B1−O1, 1.492(3); C2−C9, 1.338(4); C9−C8, 1.492(4); C8−C7, 1.342(4); C7−O1, 1.350(3); C1−P1−C3, 103.5(1); C4−B1−O1, 108.0(2); C1−C2−C9, 118.3(2); C2−C9−C8, 119.0(3); C3−C8−C7, 120.0(2); C8−C7−O1, 125.5(2).

In solution, compound **16** features ^{13}C NMR signals of the dienolate at δ 159.3 ($^{3}J_{PC}$ = 11.5 Hz, C7[O]), δ 97.9 ($^{2}J_{PC}$ = 11.2 Hz, C8), δ 145.0 ($^{3}J_{PC}$ = 12.0 Hz, C9) and δ 117.6 ($^{2}J_{PC}$ = 11.1 Hz, C2). It shows the ^{19}F NMR resonances of the pair of diastereotopic C_6F_5 groups at boron and heteronuclear magnetic resonance signals at δ 27.3 (^{31}P) and δ −3.1 (^{11}B), respectively.

The substituent pattern of the product **16** indicates that the original C2═C3 carbon−carbon double bond of the starting material **4c** becomes broken during this specific reaction course. This can be rationalized by assuming reaction sequence (see Scheme 7) that initially follows the typical phospha-Claisen pathway, similar as we had described it by our DFT calculation for the formation of compound **12** (see above). The reaction is potentially again initiated by formation of the allenic boron enolate **11b** followed by ring closure to give the intermediate **13b**. But then this "anomalous phospha-Claisen rearrangement" follows a different pathway. In this case we assume a sequence involving internal ring closure by the ylidic carbon to give **14**, followed by P−C and C2−C3 cleavage to give **15**, which then is set for formation of the final bicyclic product **16** by nucleophilic phosphane attack at the activated enone functionality of the intermediate **15** (see Scheme 7).[17,18] This anomalous phospha-Claisen sequence would consequently represent a carbon−carbon bond activating reaction within the phosphane/borane pair[19] derived from the initial frustrated Lewis pair framework.

Actually the thermolysis of the isolated allenic compound **11a** (see Scheme 5) (9 h, 60 °C, C_6D_6) gave two products. The major component seems to have a composition analogous to compound **16** (for details, see the Supporting Information).

CONCLUSIONS

The aza-Claisen reaction as described by Vedejs and Gingras[1] converts allylamines with the aid of acetylene dicarboxyate ester to amino substituted pentadiene systems. This carbon−carbon bond forming addition/rearrangement sequence was shown to be acid catalyzed. It has remained unresolved whether the actual C−C bond forming step is taking place concertedly ([3,3]sigmatropic rearrangement)[20] or rather constitutes a stepwise sequence, e.g., involving nucleophilic enolate attack at the allyl ammonium moiety.

We have now shown that the phospha-Claisen reaction can be achieved similarly to give phosphanyl substituted pentadienes. In our case, we have made use of the allylphosphane functionality inside the easily available unsaturated C_4-bridged P/B FLPs.[7] These systems provide both the allylphosphane reagent and the necessary activating Lewis acid component[21] at the same time. Consequently, we found that a series of phospha-Claisen reactions could be carried out under mild conditions by treating the P/B FLPs with a variety of acetylenic esters or ketones. Similar to the aza-Claisen reaction our phospha-Claisen sequence apparently involves initial formation of an allenic ester (or ketone derived) enolate,[11] formed in our case by phosphane nucleophile attack at the borane activated acetylenic carbonyl compound. In one case we were actually able to isolate such a 10-membered heterocyclic allylphosphonium/allenic boron enolate product and characterize it by spectroscopy and X-ray diffraction.

We note that the actual outcome of the phospha-Claisen reaction scheme seems to critically depend on the groups and substituents used. The phospha-Claisen reaction sequence seems to be special in the way that it may encounter specific situations leading to "anomalous phospha-Claisen" products. Our DFT analysis on the rearrangement of the cyclic phosphonium allenic enolate **7d** seems to indicate a stepwise pathway of the phospha-Claisen rearrangement in these special systems via the intermediates **13** instead of a direct **7** to **8** interconversion. Cleavage of the P−C1 bond inside the alleged intermediates **13** would provide a pathway to the phospha-Claisen products that were actually observed in most cases. Alternative nucleophilic enolate or P-ylide attack at C2 would in the few observed cases open the competing pathways to the "anomalous phospha-Claisen" products **12** and **16**, respectively.

EXPERIMENTAL SECTION

Typical Procedure of a Phospha-Claisen Rearrangement. A solution of compounds **4a** (102.3 mg, 0.15 mmol) and **5b** (21.3 mg, 0.15 mmol) in pentane (3 mL) was stirred at room temperature for 1 h. Then all volatiles were removed in vacuo and the residue was washed with cold pentane (3 × 1 mL). After drying in vacuo compound **8b** (102.6 mg, 83%) was obtained as an orange solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **8b** in dichloromethane at −35 °C. Decomp. (DSC): 179 °C. Anal. Calcd. for $C_{41}H_{36}BF_{10}O_4P$: C, 59.73; H, 4.40. Found: C, 59.11; H, 4.22.

Synthesis of Compound ***12***. A solution of compounds **4b** (111.6 mg, 0.2 mmol) and **5b** (28.4 mg, 0.2 mmol) in pentane (2 mL) was stirred at room temperature for 3 h. Then all volatiles were removed in vacuo and the resulting residue was washed with cold pentane (3 × 1 mL). After drying in vacuo compound **12** (119.6 mg, 85%) was obtained as a light yellow solid (two isomers 85:15 (^1H)). Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **12** in dichloromethane at −35 °C. Decomp. (DSC): 201 °C. Anal. Calcd. for $C_{31}H_{32}BF_{10}O_4P$: C, 53.16; H, 4.61. Found: C, 53.29; H, 4.61.

Synthesis of Compound ***16***. A solution of compounds **4c** (119.6 mg, 0.2 mmol) and **9b** (19.2 mg, 0.2 mmol) in toluene (2 mL) was stirred at 60 °C for 3 days. Then all volatiles were removed in vacuo and the resulting residue was washed with cold pentane (3 × 1 mL).

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After drying in vacuo, compound **16** (101.5 mg, 73%) was obtained as a light yellow solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of compound **16** in dichloromethane at −35 °C. Mp (DSC): 195 °C. Anal. Calcd. for $C_{35}H_{26}BF_{10}OP$: C, 60.54; H, 3.77. Found: C, 60.75; H, 3.93.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04046.

Experimental, analytical, and computational details (PDF)

Geometries of compounds using TPSS functional (ZIP)

Crystal structure data for **8a**, **8b**, **11a**, **12**, and **16** (CIF)

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Notes

The authors declare no competing financial interest.

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