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Alkyne 1,1-Hydroboration to a Reactive Frustrated P/B-H Lewis Pair.

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Abstract: The Mes₂P-C \equiv C-SiMe₃ alkyne reacts with the borane H₂B-Fmes by means of a rare 1,1-hydroboration reaction to give an unsaturated C₂-bridged frustrated P/B-H Lewis pair. Most of its reactions are determined by the presence of the B-H functionality at the FLP function and the activated connecting carbon-carbon double bond. It reduces carbon monoxide to the formyl stage. With nitriles it reacts in an extraordinary way: it undergoes a reaction sequence that eventually results in the formation of a P-substituted 2,3-dihydro-1*H*-1,2-azaborole derivative. Several similar examples were found. In one case a P-ylide was isolated that was related to an intermediate of the reaction sequence. It subsequently opened in an alternative way to give an alkenyl borane product. We have now treated the functionalized alkyne 1 with our recently developed H₂B-Fmes reagent 4 [Fmes: 2,4,6-tris(trifluoromethyl)-phenyl]^[10] and found that it underwent the rare 1,1-hydroboration reaction cleanly under mild conditions as well. This resulted in a specifically functionalized vicinal frustrated Lewis pair, namely the P/B-H system **5**. This gave rise to a number of rather uncommon FLP reactions, often governed by the presence of the reactive B-H function. First representative examples of this development will be described in this account.

Results and Discussion

Introduction

Alkenylboranes can conveniently be obtained from the common hydroboration reaction of alkynes. The reaction is usually a cis-1,2-B-H addition of the borane reagent^[1], but there are also some trans-1,2-hydroboration reactions known, which are mostly metal catalyzed.^[2] Much less common is the 1,1-hydroboration reaction.^[3,4] Here both the hydrogen atom and the -BR₂ rest from the respective H-BR₂ reagent end up at the same carbon atom of the former acetylene substrate and, consequently, an alkyne substituent had to undergo a 1,2-migration along the alkyne framework during this process. The 1,1-hydroboration may be viewed as a special variant of the more common 1,1carboboration reaction,^[5] a more and more important alternative method of preparation of alkenylboranes.^[6,7] Scheme 1 shows a recent 1,1-hydroboration example from our group^[4] which made use of the reactive $HB(C_6F_5)_2$ borane^[8] as the specific reagent for the alkyne to alkenyl borane conversion. The resulting 1,1hydroboration product 3 is a frustrated Lewis pair (FLP)^[9] and it underwent a variety of typical FLP reactions.



Scheme 1. An early example of the 1,1-hydroboration reaction.

Formation of the P/B-H FLP and first typical reactions

The recently introduced H₂B-Fmes reagent **4** was isolated either as a donor free doubly H-bridged dimer (**4**)₂ or as a monomeric dimethylsulfide adduct (**4**·SMe₂).^[10a] It was used for the synthesis of new frustrated Lewis pairs and also as a reagent in a new multicomponent synthesis of 1,3-dihydro-1,3-azaborinine heteroarene derivatives.^[10b] In both synthetic procedures compound **4** served as a reactive reagent in a conventional cis-1,2-hydroboration reaction. With the phosphanyl, silyl-substituted acetylene **1** the H₂B-Fmes reagent reacted differently, namely by a rarely observed 1,1-hydroboration.

The alkyne **1** was reacted for 3 h at r.t. in CD₂Cl₂ solution with one molar equiv. of **4**·SMe₂. This gave a high conversion to the product **5**. It was not isolated but *in situ* characterized by NMR spectroscopy. It features a ³¹P NMR resonance at δ 16.8 (with ³J_{PH} ≈ 116 Hz coupling to C2-H at the C₂-bridge) and a ¹¹B NMR signal at δ 3.6. This indicates the presence of P····B contact. There is a broad borane B-H ¹H NMR signal at δ 4.76. The ¹H NMR C2-H signal is found at δ 8.26 with the large ³J_{PH} coupling constant [¹³C: δ 185.7 (C2), 145.3 (¹J_{PC} ≈ 18 Hz)].

Compound **5** splits dihydrogen^[11] under mild conditions. The P/B-H FLP **5** was generated *in situ* in pentane (4h, r.t.) and the resulting solution exposed to dihydrogen (1.5 bar, r.t., 18h). Cooling of the concentrated solution (-35°C, ca 15h) gave compound **6** as a colourless solid, which was isolated in 76% yield. The X-ray crystal structure analysis (Fig. 1) showed the close to coplanar P1-C1=C2-B1 framework with the silyl substituent at carbon atom C1. The P(H)Mes₂ and B(H)₂Fmes substituents are cis-arranged at the central C=C unit. The ¹H NMR spectrum

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shows the broad 1:1:1:1 quartet of the BH₂ moiety at 2.08 and the PH signal at δ 8.71 (¹*J*_{PH} ≈ 501 Hz; ³¹P: δ -29.1). The ¹¹B NMR spectrum features a triplet of doublets at δ -22.3 with ¹*J*_{BH} ≈ 86 Hz and *J*_{PB} ≈ 26 Hz. The mesityl groups at phosphorus show hindered rotation (six ¹H NMR methyl singlets) and we observed the typical Fmes signals [δ 7.95 (s, ¹H), δ -58.4 and -62.9 (¹⁹F)].

Mes₂P--SiMe₃ + FmesBH₂·SMe₂ 4.SMe2 Me₃S Me₃S -Fmes Mes₂P Mes₂ Fmes н 5 со Me₃Si Me₃Si mes mes Mes Mesa Ъ ö 8

Scheme 2. Formation of the 1,1-hydroboration product **5** and its reaction with dihydrogen and with carbon monoxide.



Figure 1. A view of the molecular structure of the H_2 -splitting product 6 (thermal ellipsoids at 30 % probability). Selected bond lengths (Å) and angles (°): C1-C2 1.356(2), C1-P1 1.789(2), C2-B1 1.605(2), B1-C31 1.631(3), P1-H1 1.26(2), B1-H1A 1.13(2), B1-H1B 1.14(2), P1-C1-C2 112.9(1), C1-C2-B1 128.5(2), P1-C1-C2-B1 -8.2(2).

B-H boranes do not reduce carbon monoxide unless catalysed.^[12] Instead they form borane carbonyls.^[13,14] The special conditions at some P/B frameworks had previously assisted the reduction of CO with the B-H function from various sources. The P/B-H FLP **5** reacted directly with CO and reduced it to the formyl stage.^[15,16] We treated the *in situ* generated FLP **5** in pentane with carbon monoxide (1.5 bar, r.t., 18h) and isolated the product **8** as a crystalline solid in 70% yield. Compound **8** was characterized by C,H elemental analysis, by spectroscopy and by X-ray diffraction. The X-ray crystal structure analysis (Fig.2) shows the heterobicyclo[3.1.0]hexene type framework of compound **8**. It contains the newly formed unsaturated C₃PB-five membered ring with the Fmes substituent at boron, a pair of mesityl groups at phosphorus and the Me₃Si substituent at carbon atom C1 of the endocyclic double bond. Carbon atom C6 bears the hydrogen



atom and the oxygen atom O1. The formyl group is found σ -

bonded through C6 to phosphorus and n²-bonded through C6 and

O1 to boron. We note that in this arrangement the sum of the three

B1-C2/C6/C31 angles is close to 360° and the oxygen atom

resides almost symmetrically above the B1-C6 bond.

Figure 2. A view of the η²-formyl P/B compound **8** (thermal ellipsoids at 30% probability). Selected bonds lengths (Å) and angles (°): C1-C2 1.360(2), B1-C2 1.601(2), B1-C6 1.590(2), B1-C31 1.618(2), C6-O1 1.429(2), B1-O1 1.487(2), C6-O1-B1 66.1(1), O1-B1-C6 55.2(1), B1-C6-O1 58.7(1), P1-C1-C2-B1 -8.3(2), ΣB1^{CCC} 357.2.

In solution compound **8** shows a ³¹P NMR signal at δ 29.5 (dd with ³*J*_{PH} = 62.7 Hz and ²*J*_{PH} = 45.3 Hz at 233 K in CD₂Cl₂). The newly formed [P]*CH*(O)[B] unit shows up at δ 3.02 (d, ¹H) and 46.7 (¹*J*_{PC} \approx 62 Hz, ¹³C), respectively. Compound **8** shows a ¹¹B NMR resonance at δ -7.2 (299K). We assume a reaction pathway that involves cooperative P/B addition to the CO carbon atom to generate the intermediate **7**, a typical FLP reaction that has precedence.^[17]

Following the reaction directly by NMR spectroscopy at low temperature (193 K) led to the detection of an intermediate compatible with the assumed structure of compound **7**. It showed the heteroatom resonances at δ -9.7 (³¹P) and δ -16.1 (¹¹B), with mutual coupling constants of ca. 85 Hz (measured at 273 K in CD₂Cl₂), which is typical for this type of compounds.^[17c] The olefinic C2-H ¹H NMR signal of compound **7** occurs at δ 8.61 with a typical large ³J_{PH} = 51.1 Hz coupling constant. The ¹³C NMR carbonyl resonance was located at δ 228.5. Warming of the reaction mixture to 288 K resulted in a slow consumption of the intermediate, probably by internal borohydride attack at the activated carbonyl group to give the observed product **8** (see the Supporting Information for details).

Unusual reactions of the P/B-H compound 5 with organic π -systems

We reacted the P/B-H FLP **5** with a variety of reactive organic π -reagents, namely nitriles, an isocyanate and a carbodiimide. One might have assumed that in all these cases the B-H unit would simply have been used as a reductant for these reagents. That was not observed in a single case. However, we found a series of reactions, mechanistically closely related to each other, that were governed in an extraordinary way by the very special features of the conjugated phosphane/B-H moiety with a direct chemical incorporation of the connecting C=C double bond into the observed reaction pathway.

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The P/B-H FLP **5** (*in situ* generated in dichloromethane) reacted slowly with acetonitrile (r.t. 40h) to give the product **13a**. After workup involving crystallization from pentane at low temperature it was isolated crystalline in 51% yield. It was characterized by C,H,N elemental analysis, by spectroscopy and by X-ray diffraction. The X-ray crystal structure analysis (Fig. 3) revealed that a 2,3-dihydro-1*H*-1,2-azaborole derivative was obtained.^[18] Inside the core five-membered ring subunit it features a pair of planar-tricoordinate boron and nitrogen atoms. The B1-N1 linkage is short. Inside the ring there is a the C1-C6 carbon-carbon double bond that carries the PMes₂ substituent. The phosphorus coordination geometry is trigonal-pyramidal. We note that there is a saturated -CH₂- group inside the five-membered ring and the SiMe₃ group has migrated from carbon to the ring nitrogen atom.



Scheme 3. Reaction of the 1,1-hydroboration product 5 with nitriles.



Figure 3. Molecular structure of compound **13a** (R: CH₃, thermal ellipsoids at 30 % probability). Selected bonds lengths (Å) and angles (°): B1-N1 1.411(5), B1-C2 1.580(5), B1-C31 1.587(5), C1-C2 1.504(4), C1-C6 1.341(5), N1-Si1 1.776(3), ΣB1^{CCN} 360.0, ΣN1^{BCSI} 359.9, ΣP1^{CCC} 319.8.

In solution (CD₂Cl₂, 299K), compound **13a** shows the ¹H NMR signals of the ring -CH₂- group at δ 1.81 (2H) and the ring methyl substituent at δ 2.43. The ¹³C NMR signals of the three ring carbon atoms occur at δ 37.1 (CH₂), δ 117.9 (²J_{PC} = 7.8 Hz) and δ 156.4 (¹J_{PC} = 49.0 Hz). Compound **13a** shows a ³¹P NMR signal at δ -41.1 and a ¹¹B NMR resonance at δ 54.0.

Apparently, the product 13a was formed by a rearrangement process following initial acetonitrile addition to the P/B sites of the FLP 5. We assume a pathway that avoids hydride reduction of the internal C=N moiety after the addition reaction, but favors hydride attack at the activated terminus (C2) of the adjacent "enphosphonium" unit to give the ylidic intermediate 10 (Scheme 3).^[19] Addition of the ylide nucleophile at the imine electrophile would then give 11; subsequent ring opening would generate 12.^[20] We assume that the rearrangement sequence is then terminated by silyl migration from carbon to nitrogen^[21] to eventually give the observed product 13a. Several intermediates were observed by in situ NMR spectroscopy on the reaction pathway. Two successive intermediates were observed at low temperature, which can tentatively be assigned the compositions of 9a (at 193 K) and 10a (253 K, the spectra are depicted in the Supporting Information).

The reaction of the P/B-H FLP with 4-methylbenzonitrile took the analogous course and we isolated the product **13b** (R: p-tolyl) in 28 % yield (see the Supporting Information for its characterization, including the depicted solid-state structure).

The reaction of the P/B-H FLP 5 with phenyl isocyanate takes a similar route. Again, the B-H borane does not reduce the reagent after isocyanate P/B FLP addition. Instead, hydride migration to the phosphonium activated C=C double bond is favored. An intermediate was found and characterized spectroscopically at 233 K [¹¹B NMR: δ -5.1, ³¹P: δ 19.1 (t, J ~ 25 Hz), ¹³C: C=O δ 163.8 $({}^{1}J_{PC} = 104.2 \text{ Hz})]$, which we tentatively assign to compound **14**. In a subsequent rearrangement reaction, the ring carbonyl group apparently serves as the acceptor for ylidic carbon attack to generate 15 to subsequently give the first isolated product 16 (isolated in 48% yield). Thermolysis of compound 16 (toluene, 100°C ca 15 h) resulted in migration of the SiMe₃ group from carbon to oxygen to give the silvlenolether 17 (isolated in 53% yield and characterized by X-ray diffraction). Treatment of 17 with anhydrous HCl in pentane/ether then gave the bora-lactame type compound 18 (isolated in 68% yield and also characterized by Xray crystal structure analysis). Compound 18 underwent hydrolytic cleavage of the N-B linkage upon chromatography at silicagel (see the Supporting Information for the characterization of all these compounds).



Scheme 4. Unusual reaction of the 1,1-hydroboration product 5 with phenyl isocyanate.

The outcome of the reaction of the P/B-H FLP ${\bf 5}$ with N,N-bis(p-tolyl)carbodiimide provided direct experimental evidence for the

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involvement of endocyclic phosphorus ylides in this chemistry. We reacted a sample of the *in situ* generated P/B-H FLP **5** with the bis(p-tolyl)carbodiimide reagent (pentane, r.t., 20h) and isolated the product **20** after workup as a deep red crystalline material in 41% yield. Compound **20** was characterized by C,H,N elemental analysis, by spectroscopy and by a X-ray crystal structure analysis.



Scheme 5. Formation of a cyclic phosphorus ylide in the reaction of the 1,1-hydroboration product 5 with bis(p-tolyl)carbodiimide.

X-ray diffraction revealed that a six-membered heterocycle had been formed. In compound **20** the former carbodiimide nitrogen atom N1 is found coordinated to boron. The B-H hydrogen had been shifted from the boron atom B1 to the adjacent carbon atom C2 making an endocyclic methylene group. The phosphorus atom P1 has become part of an endocyclic phosphorus ylide. The P-C1 linkage is short (P1-C1: 1.677(3) Å vs P1-C6 1.855(3) Å). The six-membered heterocycle is completed by carbon atom C6 which is part of the exocyclic N-arylimine moiety (Fig. 4).

In solution (CD₂Cl₂, 193 K) compound **20** shows the ³¹P NMR resonance at δ -1.3 and the ¹³C NMR signal of the adjacent ylidic carbon atom (C1, Scheme 5, Fig. 4) at 3.9 (with ¹J_{PC} = 89.7 Hz). The ring methylene carbon resonance is at δ 21.5 (¹H: δ 2.19 and 1.91). Compound **20** shows a ¹¹B NMR signal at δ 48.7 (299K).

Thermolysis of compound **20** led to ring opening. We kept a solution of compound **20** in toluene for 3 days at 100°C. After workup we isolated the acyclic product **22** as a yellow crystalline solid in 46% yield. It was characterized by C,H,N elemental analysis, temperature dependent NMR spectroscopy and by X-ray diffraction. We assume a reaction pathway that again utilizes the nucleophilicity of the ylidic carbon atom C1. In the examples described above, this attacked an electrophilic carbon atom on the other side of the ring in the α -position to phosphorus. That pattern could also have been featured here, but the system apparently favors ylide carbon attack at the Lewis acidic boron center,^[22] thereby forming a borata-cyclopropane instead of the phosphonia-cyclopropane alternative. The allegedly resulting intermediate **21** (Scheme 5) then opens in the usual way by C-B and C-P bond cleavage to form the observed product **22**.

The X-ray crystal structure analysis of compound **22** consequently shows the newly formed geminally boryl/silyl substituted C1=C2 olefinic moiety (Fig. 5). The compound shows the short N1-B1 linkage. The coordination geometry at the nitrogen atom N1 is trigonal-planar. The C6-N1 bond is long (1.440(2) Å whereas the adjacent C6-N2 linkage is short (1.269(2) Å).

In solution (d₈-toluene) compound **22** showed a somewhat complicated behavior. At high temperature (368 K) we observed the ¹H NMR signals of the newly formed =CH₂ unit at δ 6.33 and 6.02 [¹³C: δ 140.1 (=CH₂), δ 154.6 (=C[Si][B])] and the ³¹P NMR resonance at δ -24.8. We notice that at this temperature there is only a single set of NMR resonances for the pair of p-tolyl groups at the two nitrogen atoms. We interpret this observation as an indication for the rapid boryl migration between these two nitrogen centers^[17a,23] under these condition at the NMR time scale. A decoalscence was observed upon decreasing the temperature of the NMR measurements (the spectra are depicted in the Supporting Information)



Figure 4. Molecular structure of the ylidic compound **20** (only one of the two chemically equivalent molecules found in the crystal is shown, thermal ellipsoids shown at 30% probability). Selected bonds lengths (Å) and angles (°): P1-C1 1.677(3), P1-C6 1.858(3), P1-C11 1.868(3), P1-C21 1.831(3), C1-C2 1.534(4), B1-C2 1.554(4), B1-N1 1.727(4), N1-C41 1.459(4), N1-C6 1.419(4), C6-N2 1.273(4), N2-C51 1.419(4), ΣB1^{CCN} 360.0, ΣN1^{BCC} 359.8, C6-N2-C51 123.4(3).



Figure 5. A view of the molecular structure of compound **22** (with thermal ellipsoids at 30% probability). Selected bond lengths (Å) and angles (°): C1-C21 1.340(3), B1-C2 1.575(2), B1-N1 1.424(4), N1-C41 1.455(2), C6-N1 1.440(2), C6-N2 1.269(2), N2-C51 1.411(2), C6-P1 1.862(2), C6-N2-C51 127.1(2), ΣB1^{NCC} 359.9, ΣN1^{BCC} 360.0, ΣP1^{CCC} 332.4.

We found some unexpected evidence for the possible presence of a borata-cyclopropane structure from the reaction of the P/B-H FLP with p-tolylacetylene. Addition of the terminal alkyne to a yellow solution of the *in situ* generated P/B-H FLP **5** (pentane, r.t.) immediately give a red solution from which an off-white solid crystallized over a period of ca. 15h at r.t. The solid product was isolated in 55% yield. The X-ray crystal structure analysis

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revealed the presence of the conventional FLP alkyne C-H activation product^[24] **23** (Fig. 6 and Scheme 6). It showed the typical framework of the unsaturated C₂-bridged P/B framework. Both the phosphorus and the boron atom bear a hydrogen substituent. The p-tolylethynyl rest is found attached at the boron atom B1.



Scheme 6. Reaction of the 1,1-hydroboration product 5 with p-tolyl acetylene.



Figure 6. A projection of the structure of the alkyne reaction product 23 in the crystal (thermal ellipsoids are depicted at 15 % probability). Selected bonds lengths (Å) and angles (°): P1-C1 1.790(5), C1-C2 1.340(8), C2-B1 1.623(8), B1-C41 1.584(8), C41-C42 1.218(8), C2-B1-C41 116.8(5), B1-C41-C42 175.9(6), C41-C42-C43 178.1(6).

We dissolved compound **23** in d₈-toluene to obtain its spectroscopic parameters. However, the NMR spectra indicated that the compound had rearranged during this process. We assume that the rearranged product **25** featuring a boratacyclopropane substructure is present in solution. We still observed the typical signals of the Mes₂PH-⁺ phosphonium unit [³¹P: δ -4.1 (¹J_{PH} ≈ 503 Hz) at 233 K] and the p-tolylethynyl substituent at boron [¹³C: δ 106.7 (=C-B), δ 102.3 (=C-p-Tol)]. In addition, we observed the ¹H NMR signals of a pair of diastereotopic hydrogen atoms of a methylene group adjacent to boron [δ 1.92 and δ 1.45 (dd, ³J_{PH} = 33.7 Hz, ²J_{HH} = 9.1 Hz), each 1H]. The ¹³C NMR signals of the C₂-bridge in **25** occur at δ 21.7 [*C*2H₂ (²J_{PC} = 10.9 Hz)] and δ -5.3 [C1 (br d, ¹J_{PC} ≈ 30 Hz)] at 233 K. At 299 K, it shows a broad ¹¹B NMR feature at δ -17.6. The

alleged compound **25** has a pair of chirality centers (C1, B). It shows dynamic NMR spectra. Compound **25** shows some broad NMR signals at 299 K; sharp signals were monitored at 233 K. At this temperature two ¹H NMR Me₃Si-singlets were observed in a 1:10 intensity ratio.

Thermolysis of compound **25** (toluene, 100°C, 4h) resulted in a typical ring-opening of the borata-cyclopropane^[25] with fragmentation. Rupture of the B-C2 and C1-P linkages gave the "enyne-borane" **26** plus dimesitylphosphane (Scheme 6). Compound **26** was isolated in 79% yield. It was characterized by an X-ray crystal structure analysis and by spectroscopy (see the Supporting Information for details).

Conclusion

Unsaturated vicinal FLPs are often prepared by means of 1,1carboboration reactions of suitably substituted alkynes.^[26] We have here used a rarely encountered relative, namely the 1,1hydroboration reaction. In our case a hydrogen and the remaining -B(H)Fmes moiety from the H₂B-Fmes reagent have become connected to the same carbon atom of the former alkyne substrate. This resulted in the formation of a unique C₂-bridged frustrated Lewis pair bearing a bulky Mes₂P substituent at one end and a reactive -B(H)Fmes group at the other end of the unsaturated C₂-bridge. In the CO reaction this led to a typical frustrated Lewis pair behaviour: The B-H functional group cannot reduce the carbon monoxide molecule directly, but upon P/B FLP CO activation the generated hydridoborate functionality can use its hydride for carbonyl attack^[15] and formation of the observed η^2 formyl B/P product.



Scheme 7: General scheme of reactions of the 1,1-hydroboration product 5 with some organic π -reagents.

The reactions of the organic π -reagents employed in this study with the P/B-H FLP could have followed a principally similar route, but they did not. Here the P/B FLP addition reaction opened a favorable alternative pathway. Both the B-H functionality and the bridging activated olefinic C=C bond determined the reactivity of

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the FLP 5 toward these reagents to a considerable extent. The in situ generated alkenyl phosphonium function in the P/B-H FLP adducts of nitriles, isocyanate or carbodiimide is prone to nucleophilic attack - here by the simultaneously generated borohydride - to generate the respective phosphorus ylide functional group inside the newly formed heterocyclic ring system. This type of an intermediate was observed spectroscopically in some cases. In one example we could even isolate such a compound and characterize it structurally by X-ray diffraction. A specific feature of the here encountered systems is that the Pylides "find" an intramolecular electrophile to initiate a subsequent rearrangement process. In the nitrile and isocyanate cases this led to ring contraction and formation of the 2,3-dihydro-1H-1,2azaborole derivatives; in the carbodiimide case (and in the case of the FLP/p-tolylacetylene reaction product) this led to ylidic attack at the internal boron electrophile followed by fragmentation. We note that the specific introduction of a B-H functionality in cooperation with the unsaturated C₂-bridge opens some rather unusual reaction pathways in the FLP-derived chemistry. We will see how the principles found in these pathways can be utilized for the further development of simple ways of preparing novel interesting product types.

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Keywords: boron • phosphorus • rearrangement • fragmentation • ylide

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RESEARCH ARTICLE

Entry for the Table of Contents



Table of Contents: A P/B-H frustrated Lewis pair is formed by means of a rare 1,1-hydroboration reaction. It reacts in an unusual way with a variety of organic π -systems by addition/rearrangement routes.