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RESEARCH ARTICLE

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

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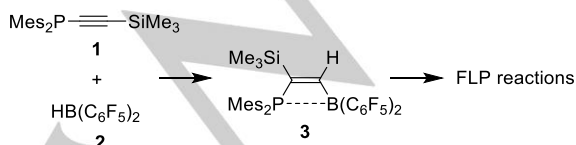
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Abstract: The $\text{Mes}_2\text{P}-\text{C}\equiv\text{C}-\text{SiMe}_3$ alkyne reacts with the borane $\text{H}_2\text{B}-\text{Fmes}$ by means of a rare 1,1-hydroboration reaction to give an unsaturated C_2 -bridged frustrated P/B-H Lewis pair. 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 $\text{H}_2\text{B}-\text{Fmes}$ 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.

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 $-\text{BR}_2$ rest from the respective $\text{H}-\text{BR}_2$ 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 1,1-carboboration 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 $\text{HB}(\text{C}_6\text{F}_5)_2$ borane^[8] as the specific reagent for the alkyne to alkenyl borane conversion. The resulting 1,1-hydroboration 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.

Results and Discussion

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

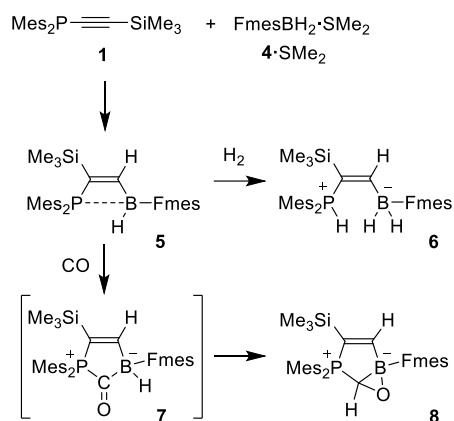
The recently introduced $\text{H}_2\text{B}-\text{Fmes}$ reagent **4** was isolated either as a donor free doubly H-bridged dimer (**4**)₂ or as a monomeric dimethylsulfide adduct (**4**· SMe_2).^[10a] It was used for the synthesis of new frustrated Lewis pairs and also as a reagent in a new multi-component 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 $\text{H}_2\text{B}-\text{Fmes}$ reagent reacted differently, namely by a rarely observed 1,1-hydroboration.

The alkyne **1** was reacted for 3 h at r.t. in CD_2Cl_2 solution with one molar equiv. of **4**· SMe_2 . This gave a high conversion to the product **5**. It was not isolated but *in situ* characterized by NMR spectroscopy. It features a ^{31}P NMR resonance at δ 16.8 (with $^3J_{\text{PH}} \approx 116$ Hz coupling to C2-H at the C_2 -bridge) and a ^{11}B NMR signal at δ 3.6. This indicates the presence of $\text{P}\cdots\text{B}$ 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 $^3J_{\text{PH}}$ coupling constant [^{13}C : δ 185.7 (C2), 145.3 ($^1J_{\text{PC}} \approx 18$ Hz)].

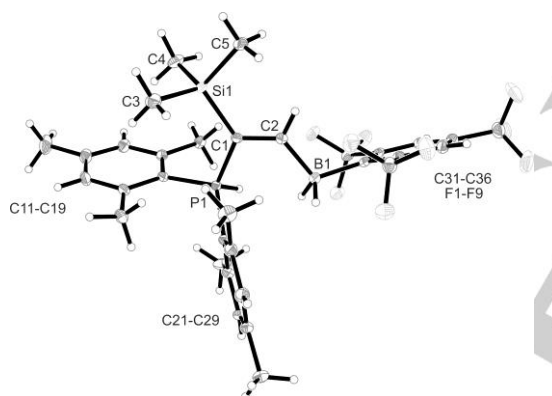
Compound **5** splits dihydrogen^[11] under mild conditions. The P/B-H FLP **5** was generated *in situ* in pentane (4h, r.t.) and the resulting solution exposed to dihydrogen (1.5 bar, r.t., 18h). Cooling of the concentrated solution (-35°C , ca 15h) gave compound **6** as a colourless solid, which was isolated in 76% yield. The X-ray crystal structure analysis (Fig. 1) showed the close to coplanar $\text{P1}-\text{C1}=\text{C2}-\text{B1}$ framework with the silyl substituent at carbon atom C1. The $\text{P}(\text{H})\text{Mes}_2$ and $\text{B}(\text{H})_2\text{Fmes}$ substituents are *cis*-arranged at the central $\text{C}=\text{C}$ unit. The ^1H NMR spectrum

RESEARCH ARTICLE

shows the broad 1:1:1:1 quartet of the BH₂ moiety at 2.08 and the PH signal at δ 8.71 ($^1J_{\text{PH}} \approx 501$ Hz; ^{31}P : δ -29.1). The ^{11}B NMR spectrum features a triplet of doublets at δ -22.3 with $^1J_{\text{BH}} \approx 86$ Hz and $J_{\text{PB}} \approx 26$ 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 (^{19}F)].

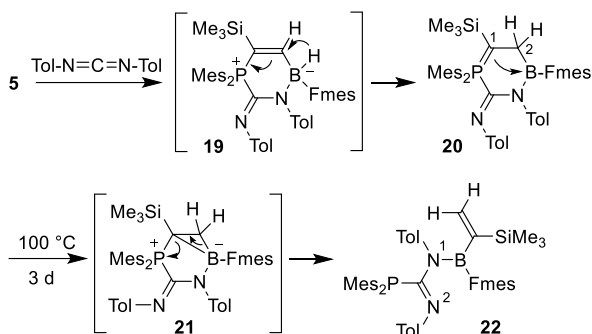


Scheme 2. Formation of the 1,1-hydroboration product **5** and its reaction with dihydrogen and with carbon monoxide.



RESEARCH ARTICLE

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 decoupling was observed upon decreasing the temperature of the NMR measurements (the spectra are depicted in the Supporting Information)

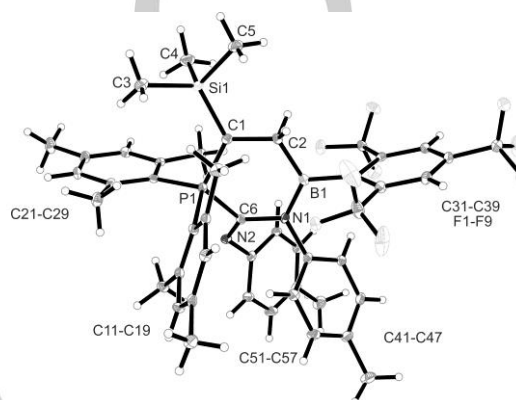


Figure 4. Molecular structure of the ylidic compound **20** (only one of the two chemically equivalent molecules found in the crystal is shown, thermal ellipsoids shown at 30% probability). Selected bond lengths (Å) and angles (°): P1-C1 1.677(3), P1-C6 1.858(3), P1-C11 1.868(3), P1-C21 1.831(3), C1-C2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

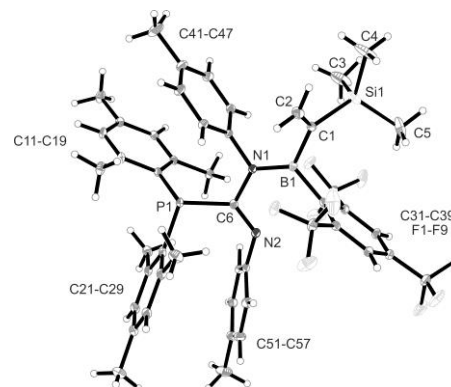
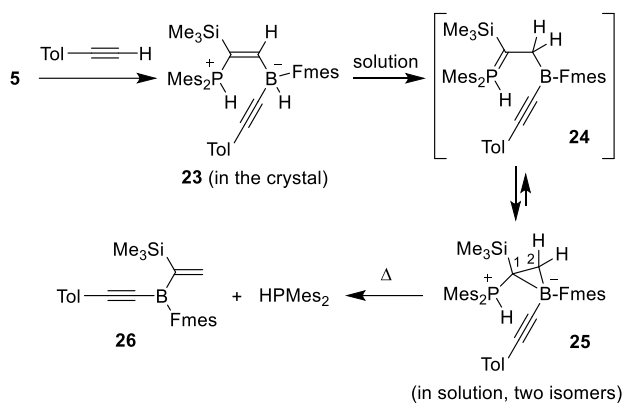


Figure 5. A view of the molecular structure of compound **22** (with thermal ellipsoids at 30% probability). Selected bond lengths (Å) and angles (°): C1-C21 1.340(3), B1-C2 1.575(2), B1-N1 1.424(4), N1-C41 1.455(2), C6-N1 1.440(2), C6-N2 1.269(2), N2-C51 1.411(2), C6-P1 1.862(2), C6-N2-C51 127.1(2),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

RESEARCH ARTICLE

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-tolylolethynyl rest is found attached at the boron atom B1.



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

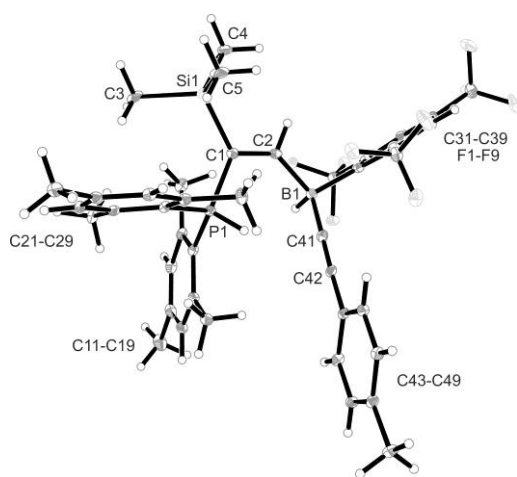


Figure 6. A projection of the structure of the alkyne reaction product **23** in the crystal (thermal ellipsoids are depicted at 15 % probability). Selected bonds lengths (Å) and angles (°): P1-C1 1.790(5), C1-C2 1.340(8), C2-B1 1.623(8), B1-C41 1.584(8), C41-C42 1.218(8), C2-B1-C41 116.8(5), B1-C41-C42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

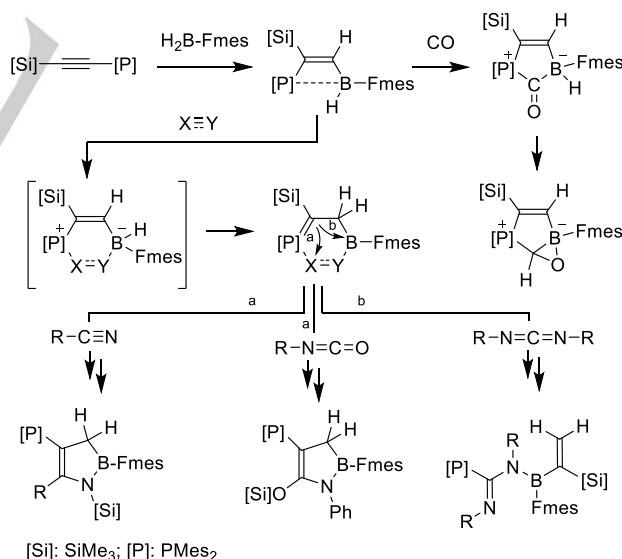
We dissolved compound **23** in d₈-toluene to obtain its spectroscopic parameters. However, the NMR spectra indicated that the compound had rearranged during this process. We assume that the rearranged product **25** featuring a borata-cyclopropane substructure is present in solution. We still observed the typical signals of the Mes₂PH⁺ phosphonium unit [³¹P: δ -4.1 (¹J_{PH} ≈ 503 Hz) at 233 K] and the p-tolylolethynyl 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 [C2H₂ (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 1,1-carboboration reactions of suitably substituted alkynes.^[26] We have here used a rarely encountered relative, namely the 1,1-hydroboration 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 η²-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

RESEARCH ARTICLE

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 P-ylides “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-1*H*-1,2-azaborole 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

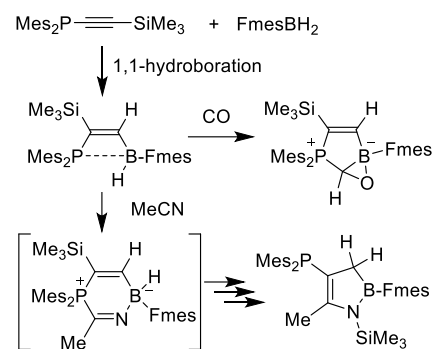


Table of Contents: A P/B-H frustrated Lewis pair is formed by means of a rare 1,1-hydroboration reaction. It reacts in an unusual way with a variety of organic π -systems by addition/rearrangement routes.