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Cooperative reaction chemistry derived from a borata-diene framework†

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The bifunctional frustrated BH^-/B hydridoborate nucleophile/borane Lewis acid pair **6** is prepared starting from the borata-diene **3** by a sequence of sequential protonation/hydride attachment, followed by hydroboration with Piers' borane $[\text{HB}(\text{C}_6\text{F}_5)_2]$. The *trans*-1,2-bifunctional system **6** reduced carbon monoxide eventually to the aldehyde product **10**.

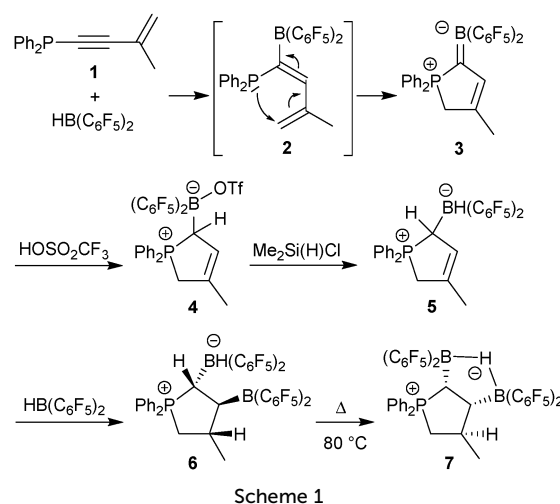
Borohydrides are important reducing reagents. However, some of these systems show rather low hydride nucleophilicities, especially when additional strongly electron-withdrawing substituents are attached at the boron center.¹ Lewis acid assistance is often helpful or even essential.² We have now prepared a bifunctional $-\text{B}(\text{C}_6\text{F}_5)_2\text{H}^-/-\text{B}(\text{C}_6\text{F}_5)_2$ borohydride/borane Lewis acid pair by selective construction starting from a readily available borata-diene precursor. The functionalities were separated similarly as it had previously been achieved in frustrated Lewis pair chemistry at rigid frameworks. The $-\text{B}(\text{C}_6\text{F}_5)_2\text{H}^-/-\text{B}(\text{C}_6\text{F}_5)_2$ frustrated pair showed a high reaction potential, *e.g.* for the stoichiometric conversion of carbon monoxide.³ The preparation of the active hydridoborate/borane pair and some first reactions are described in this account.

Borata-alkenes represent mesomeric structures of α -boryl carbanions⁴ and consequently they can be prepared by deprotonation of the boranes with a suitable base.⁵ This reaction is, however, in most cases problematic since the majority of conventional bases would preferentially add to the borane Lewis acid site rather than deprotonate in the α -position. Therefore, a rather limited number of borata-alkenes were prepared in this straightforward way, isolated and amply characterized. The few structurally characterized examples show a pronounced $\text{B}=\text{C}$ double bond character with boron-carbon bond lengths around 1.44 Å.⁶

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‡ X-Ray crystal structure analysis.



Scheme 1

We recently reported a base-free synthetic entry to the zwitterionic borata-diene compound **3** (see Scheme 1):^{7,8} hydroboration⁹ of the P-enyne **1** with Piers' borane $[\text{HB}(\text{C}_6\text{F}_5)_2]$ generated the geminal P/B Lewis pair **2** that underwent rapid intramolecular ring-closure to **3**.⁷ Compound **3** served as the starting material for the construction of a reactive borohydride/borane pair. Treatment of **3** with triflic acid resulted in the protonation of the incipient carbanion site in the α -position to boron and attachment of the corresponding triflate anion to the boron atom.¹⁰ The resulting Brønsted acid addition product **4** was isolated in 67% yield. Its X-ray crystal structure analysis confirmed that a selective 1,2-addition of HOSO_2CF_3 had occurred across the $\text{B}=\text{C}$ double bond. Compound **4** contains a sp^3 -hybridized carbon atom C1 in the ring and has the adjacent C2–C3 double bond intact. The triflate anion is found to be attached at the boron atom B1 (for structural details and the spectroscopic characterization of compound **4** see the ESI†).

We then exchanged the OTf group at boron for hydride. This was effected by treatment of compound **4** with excess chlorodimethylsilane (30 min, 60 °C, dichloromethane).¹⁰ The borohydride



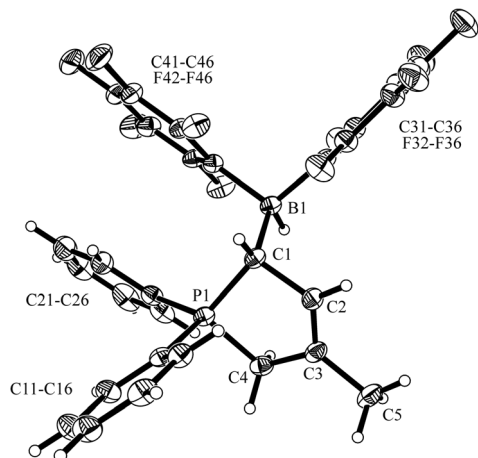


Fig. 1 Molecular structure of the phosphonium/hydridoborate compound **5** (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): C1–B1 1.668(4), C1–P1 1.789(3), C1–C2 1.523(3), C2–C3 1.319(4), C3–C4 1.503(4), C4–P1 1.804(3), C1–P1–C4 97.2(1), B1–C1–C2 110.2(2).

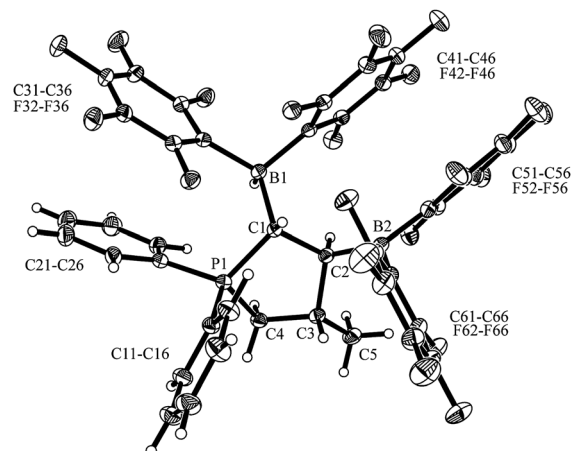


Fig. 2 Molecular structure of compound **6** (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): C1–B1 1.675(4), C1–P1 1.806(3), C1–C2 1.597(3), C2–C3 1.550(4), C3–C4 1.530(4), C4–P1 1.788(3), C1–P1–C4 97.8(1), B1–C1–C2 110.0(2).

product **5** was isolated as a colorless solid in 73% yield. It showed the broad [B]–H 1 : 1 : 1 : 1 ^1H NMR quartet at δ 2.78 ppm in $[\text{D}_2]$ -dichloromethane solution with a corresponding ^{11}B NMR signal at δ –22.1 ppm ($^1J_{\text{BH}} \sim 94$ Hz) [^{31}P NMR: δ 51.1 ppm]. The X-ray crystal structure analysis of compound **5** shows the hydridoborate substituent attached at the ring carbon atom C1 ($\sum \text{B1}^{\text{CCC}} = 331.9^\circ$). The substituent features a staggered conformation at the connecting C1–B1 vector with an anti-periplanar orientation of the H–C1–B1–H moiety. The five-membered phosphonium ring contains a distal carbon–carbon double bond (C2=C3) (see Fig. 1).

Compound **5** can formally be regarded as the 1,2-dihydrogen addition product to the borata-alkene **3**. However, it was not obtained by means of a real hydrogenation process, but rather formed in a conventional way by adding a proton to the basic borata-alkene α -carbon followed by hydride attachment at boron. Compound **5** underwent hydroboration with Piers' borane [$\text{HB}(\text{C}_6\text{F}_5)_2$] to give **6** (isolated in 63% yield).

The ^1H NMR spectrum showed the C3–CH₃ doublet at δ 1.34 ppm ($^3J_{\text{HH}} = 6.3$ Hz) which indicated regioselective formation of the anti-Markovnikov [B]–H addition product. The newly attached $\text{B}(\text{C}_6\text{F}_5)_2$ group shows a ^{11}B NMR resonance (δ 65.1 ppm) typical of a planar-tricoordinated boron Lewis acid. Consequently, this group shows only a single set of ^{19}F NMR resonances of its pair of homotopic C_6F_5 groups with a typical large p,m -signal shift difference of $\Delta\delta_{m,p} = 12.0$ ppm. The $\text{B}(\text{H})(\text{C}_6\text{F}_5)_2$ ^{11}B NMR resonance occurs at δ –16.3 ppm and this signal is split into a doublet ($^1J_{\text{BH}} \sim 77$ Hz) that indicates the presence of an unbridged terminal [B]–H hydride.

The X-ray crystal structure analysis (see Fig. 2) has confirmed the formation of the anti-Markovnikov $\text{HB}(\text{C}_6\text{F}_5)_2$ -addition product **6**, featuring the pair of boron containing substituents *trans*-vicinally attached at the carbon atoms C1 and C2 at the five-membered heterocyclic phosphonium core. The Lewis acidic $\text{B}(\text{C}_6\text{F}_5)_2$ substituent is attached at C2 ($\sum \text{B2}^{\text{CCC}} = 359.1^\circ$) whereas the $\text{B}(\text{H})(\text{C}_6\text{F}_5)_2$ group ($\sum \text{B1}^{\text{CCC}} = 332.4^\circ$) is found to be bonded

to C1. This group has retained the anti-periplanar arrangement of the H–C1–B1–H unit. Carbon atom C3 is now sp^3 -hybridized. C3–H is oriented *cis*- to the vicinal C2–B2 vector as expected from the hydroboration reaction.

The *trans*-vicinal arrangement of the borane and boryl substituents in compound **6** was probably determined by steric hindrance between these bulky groups during the hydroboration reaction. Compound **6** was formed under kinetic control. This was shown by thermolizing it subsequently. Keeping compound **6** for 3 days at 80 °C resulted in the formation of its *cis*-isomer **7** which was eventually isolated in 81% yield. We assume that it was formed by a dehydroboration/hydroboration sequence¹¹ and thus we conclude that compound **7** is the thermodynamic hydroboration product under these conditions.

Compound **7** shows a broad [B]–H signal in the ^1H NMR spectrum at δ 2.12 ppm and a pair of broad ^{11}B NMR resonances at δ 9.4 and 5.5 ppm, respectively. It shows the typical ^1H NMR –C3H–CH₃ methyl doublet at δ 0.99 ppm ($^3J_{\text{HH}} = 6.5$ Hz) and the three 1,2-*cis*-3-*trans* CH resonances at δ 4.44 (C1–H), 2.78 (C2–H) and 3.11 ppm (C3–H) (C_4H_2 : δ 3.17 and 2.35 ppm). The structure of compound **7** was confirmed by X-ray diffraction. It shows a *cis*-1,2-arrangement of the H-bridged $-\text{B}(\text{C}_6\text{F}_5)_2(\mu\text{H})\text{B}(\text{C}_6\text{F}_5)_2$ -unit at the ring carbon atoms C1 and C2 (see Fig. 3). The methyl group at C3 is *cis*-oriented to the C2–B2 vector. Both the boron atoms feature markedly distorted tetrahedral coordination geometries ($\sum \text{B1}^{\text{CCC}} = 346.9^\circ$, $\sum \text{B2}^{\text{CCC}} = 345.8^\circ$).¹²

Compound **7** represents just an example of a rather conventional hydride bridged B–H–B type compound. In contrast, compound **6** is remarkable in that it contains an unquenched pair of an active borohydride nucleophile and a strongly Lewis acidic boryl electrophile attached at adjacent carbon atoms at the central five-membered heterocyclic core structure. It is due to these specific structural features of the phosphoniacyclopentane framework that these two units are very effectively hindered from annihilating their typical reactivities by “neutralizing” bridging μ -hydride formation. In a way this situation may be regarded as a



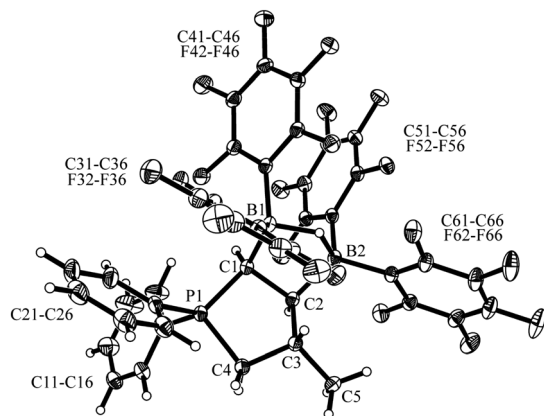
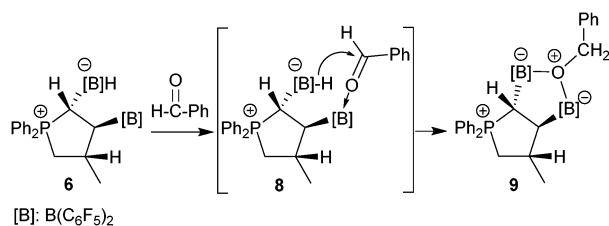


Fig. 3 Molecular structure of compound **7** (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): C1–B1 1.649(3), C1–P1 1.809(2), C1–C2 1.568(3), C2–C3 1.541(3), C3–C4 1.540(3), C4–P1 1.812(2), C1–P1–C4 98.4(1), B1–C1–C2 104.0(2).



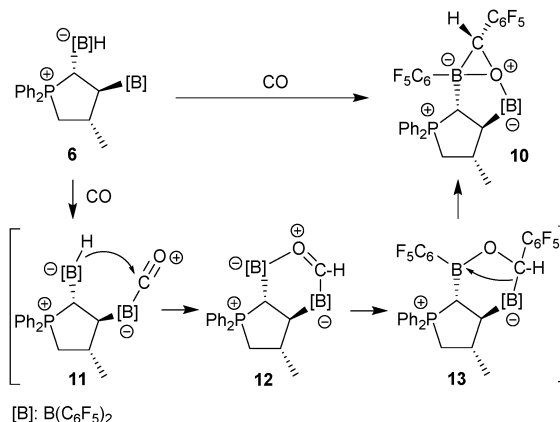
Scheme 2

new form of a frustrated Lewis pair (FLP), hereby having a pair of a hydride nucleophile and a borane Lewis acid being effectively hindered from mutual quenching by the specific nature of the framework that they are attached to. This opens the chance to find cooperative reaction with added substrates.

Reaction of the bifunctional compound **6** with benzaldehyde (r.t., 1 h) gave the reduction product **9** (isolated in 77% yield after crystallization from pentane) (see Scheme 2).¹³ The X-ray crystal structure analysis showed that hydride had been added to the carbonyl carbon atom to form the [B]-benzyl alcoholate product. The alcoholate oxygen is rather symmetrically bonded to both boron atoms. The oxygen atom shows a trigonal planar coordination geometry ($\sum \text{O1}^{\text{CBB}} = 356.9^\circ$). The boryl substituents are found to be *trans*-1,2-attached at the ring carbon atoms C1 and C3 (see the ESI† for structural details and the spectroscopic characterization of compound **9**).

Both isomers **6** and **7** were exposed to carbon monoxide. While the conventional hydride-bridged *cis*-isomer **7** was inert toward CO under our typical reaction conditions, BH[−]/B FLP **6** reduced carbon monoxide under mild reaction conditions. We exposed compound **6** in dichloromethane to carbon monoxide (2.5 bar) under close to ambient conditions (r.t., 30 min). After a short reaction time, workup gave product **10** in 63% yield (see Scheme 3). The product was characterized by C,H elemental analysis, by NMR spectroscopy and X-ray diffraction (see Fig. 4).

The X-ray crystal structure analysis (single crystals were obtained from dichloromethane/pentane) showed that CO had become reduced at the BH[−]/B framework of **6** and coupled with a



Scheme 3

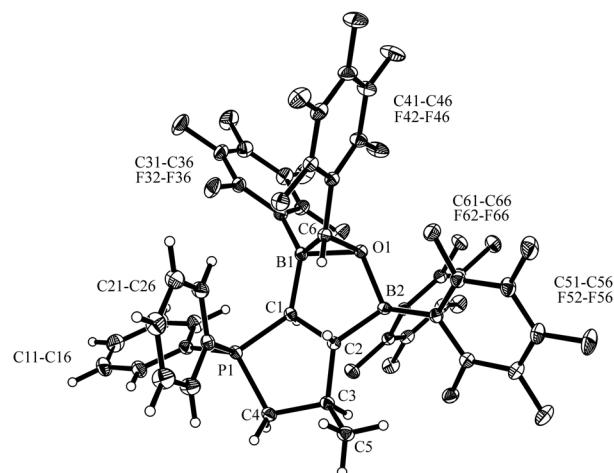


Fig. 4 A projection of the carbonylation product **10** (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): B1–O1 1.577(2), B2–O1 1.593(2), C1–B1 1.612(3), C1–P1 1.783(2), C1–C2 1.555(2), C2–C3 1.552(2), C2–B2 1.633(3), C3–C4 1.562(3), C4–P1 1.816(2), C6–O1 1.501(2), C1–P1–C4 95.8(1), B1–C1–C2 105.8(1), O1–B1–C6 57.1(1), B1–C6–O1 61.9(1), B1–O1–C6 61.0(1).

–C₆F₅ group to give a pentafluorobenzaldehyde moiety. However, this reduction product is bonded in a special manner to the framework of **6**: the newly introduced oxygen atom is found to bridge between the pair of boron atoms and the aldehyde carbon atom (which is derived from the CO molecule) is bonded to boron atom B1. So the C₆F₅–CHO unit is found η²-bonded to B1³ and κO-bonded to B2. This situation generates a rather special stereochemical situation by introducing a pair of new chirality centers, namely at the former CO carbon atom (C6) and its adjacent boron atom (B1). Together with the three carbon chiral centers of the framework (C1, C2, C3) this makes a total of five stereogenic centers present in compound **10**. Three of these (at the framework) are determined in their relative stereochemistry by the starting material **6** (which was formed as a single diastereomer), but in principle the pair of newly introduced stereocenters could have led to the formation of **10** as a mixture of four diastereomers. However, we find only a single diastereomer of **10** being formed in the carbonylation reaction of **6**. It is characterized



by a syn-arrangement of the C6 group to the C5-methyl substituent and an exo-orientation of the C6-pentafluorophenyl substituent.

In solution (CD₂Cl₂) we have observed the ¹H/¹³C NMR signals of the CO derived –CH–Ar group at δ 4.29 ppm/δ 60.8 ppm. Compound **10** shows the ¹⁹F NMR resonances of four different C₆F₅ substituents (for details see the ESI†) and we have recorded the heteronuclear magnetic resonances of the pair of boron atoms (¹¹B: δ 4.2 and –3.5 ppm) and the phosphorus atom (³¹P: δ 38.9 ppm).

It has long been known that boranes can form carbonyl adducts upon exposure to CO. The borane carbonyl H₃B–CO¹⁴ and Piers' borane carbonyl (C₆F₅)₂HB–CO¹⁵ are typical examples. Therefore, we were led to assume a reaction pathway for the formation of compound **10** that involved the reactive borane carbonyl intermediate **11**. Subsequent reduction by the adjacent borohydride reagent to the formyl stage followed by nucleophilic C₆F₅ attack would then generate the C₆F₅–CHO subunit.¹⁶ Thermodynamically driven rearrangement would then give the final product **10** (see Scheme 3).

Compound **6** contains an interesting construction principle. It contains a pair of antagonistic¹⁷ boron bound functional groups. The strongly Lewis acidic B(C₆F₅)₂ moiety is attached at carbon atom C2. It has the anionic hydridoborate moiety attached in close vicinity at its adjacent carbon atom C1. Nevertheless, these two divergent functionalities do not hinder each other's typical reactivity (e.g. by hydride bridging) because of the rigid separation caused by the typical stereochemical features of the five-membered heterocyclic framework. This allows cooperative reactions with added reagents which show a remote resemblance of the behavior of frustrated Lewis pairs. In our case the carbonyl reagents, activated by attachment at the Lewis acid site, got converted by nucleophilic hydride attack from the adjacent hydridoborate. The bifunctional BH[–]/B pair has conveniently become available by a straightforward synthetic route derived from a readily available borata-alkene starting material. Our study indicates that the general principles that have made frustrated Lewis pair chemistry successful are beginning to stretch out to related fields in the vicinity of FLP chemistry and enlarge its scope.¹⁸

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