

Research



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Author for correspondence:

Gerhard Erker
e-mail: erker@uni-muenster.de

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Design and reactions of a carbon Lewis base/boron Lewis acid frustrated Lewis pair

Jennifer Möricke, Birgit Wibbeling, Constantin

G. Daniliuc, Gerald Kehr and Gerhard Erker

Organisch-Chemisches Institut, Universität Münster,
Corrensstrasse 40, 48149 Münster, Germany

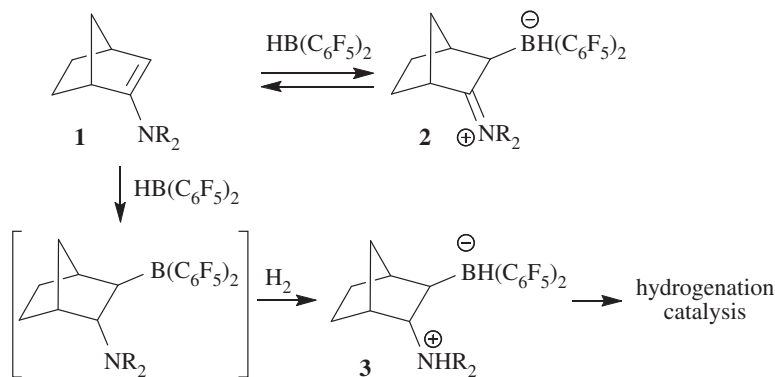
GK, 0000-0002-5196-2491; GE, 0000-0003-2488-3699

The conjugated dienamine **4** selectively adds Piers' borane $[\text{HB}(\text{C}_6\text{F}_5)_2]$ to give the enamine/borane system **5**, which features a boratirane structure by internal enamine carbon Lewis base to boron Lewis acid interaction. Compound **5** behaves as a C/B frustrated Lewis pair and undergoes typical addition reactions to benzaldehyde, several nitriles and to sulfur dioxide.

This article is part of the themed issue 'Frustrated Lewis pair chemistry'.

1. Introduction

Frustrated Lewis pairs (FLPs) undergo cooperative reactions with a variety of small molecules [1–3]. Most notably, they often split dihydrogen [4–6], and many FLPs were shown to selectively add to a variety of organic and inorganic π -systems. FLPs are composed of Lewis acid/base pairs which are effectively hindered (often in an equilibrium situation) from neutralizing Lewis adduct formation. This is mostly done by attaching very bulky substituents at both the Lewis acid and the Lewis base component of the pair. While the Lewis acid is mostly boron based [1–3] (with increasing attention on alternatives such as strongly electrophilic metal [7–10] or phosphonium systems [11]) the Lewis base component is mostly a bulky phosphane or amine [1–3] and sometimes ethers have been successfully used [12–14]. In some cases, substrates containing the group 15 heteroatoms have taken a dual role in the catalytic hydrogenation process, namely as the reagent



Scheme 1. Trapping of the non-visible N/B FLP by the H_2 -splitting reaction of the respective enamine/borane adduct **2**.

and at the same time the Lewis base [15]. It must be noted that carbon Lewis bases have seldom been used in FLP chemistry, with notable exceptions being the N-heterocyclic carbene/ $\text{B}(\text{C}_6\text{F}_5)_3$ and related systems described by Stephan, Tamm, and others [16–27] and Alcarazo's carbodiphosphorane/ $\text{B}(\text{C}_6\text{F}_5)_3$ analogues [28–32]. α -Boryl carbanions might formally be candidates for new C/B FLP developments [33,34], but usually their conjugative interaction is so pronounced that they serve as borata alkenes (with their characteristic chemistry) [35–37] rather than as FLP systems.

We thought that enamines might be interesting candidates for C/B FLP design and development, especially if such systems became available by a simple hydroboration route. However, there were some principal problems that needed to be overcome. We had previously shown that many enamines just form carbon/boron Lewis base/Lewis acid adducts (scheme 1); the adduct formation is often reversible and then allows simple enamine hydroboration to give N/B FLPs, a reaction that is often only detected by its subsequent H_2 -splitting reaction [38–41]. It requires a different substrate design to overcome this common enamine/ $\text{HB}(\text{C}_6\text{F}_5)_2$ behaviour. This we have done, and the first results of this new development are described below.

We chose the conjugated *N,N*-diisopropyl dienamine **4** as our substrate (see the electronic supplementary material for its synthesis). It bears a pair of geminal methyl groups at the terminal diene sp^2 -carbon atom and we hoped to direct the subsequent hydroboration away from the usual enamine regiochemistry. This was actually the case. We reacted a solution of the dienamine **4** in pentane with an equimolar amount of $\text{HB}(\text{C}_6\text{F}_5)_2$ [42,43]. The borane does not completely dissolve in this solvent and the hydroboration reaction takes place from the suspension that is formed. After 30 min at r.t., the reaction was complete and an orange precipitate had formed. It was isolated as a solid with a 62% yield and characterized by C,H,N elemental analysis, by spectroscopy and by X-ray diffraction (single crystals were obtained at -36°C from a toluene solution layered with pentane).

The X-ray crystal structure analysis (figure 1) shows that the hydroboration reaction of the dienamine **4** had indeed proceeded with the expected 'inversed' regiochemistry. The hydride had been added to the terminal dimethyl-substituted diene carbon atom C4 and, consequently, the $\text{B}(\text{C}_6\text{F}_5)_2$ group was bonded to the adjacent carbon atom C3. The structure of the product can probably best be described by a resonance hybrid of the mesomeric forms **5/5'** (scheme 2). The B1–C3 bond is quite short at 1.552(2) Å (cf. B1–C21/C31: 1.610(2) Å) and the B1–C3 vector leans over towards carbon atom C2 (angle C2–C3–B1: $67.8(1)^\circ$). There is clearly a bonding interaction between B1 and C2, although it is probably weak (1.726(2) Å). We note a characteristic delocalized bond lengths pattern of the remaining **5/5'** framework (C2–C3: 1.541(2) Å, C1–C2: 1.392(2) Å, N1–C1: 1.315(2) Å). The C2–H/C3–H hydrogen atoms at the distorted boratirane [44–48] ring are *trans*-oriented at the framework.

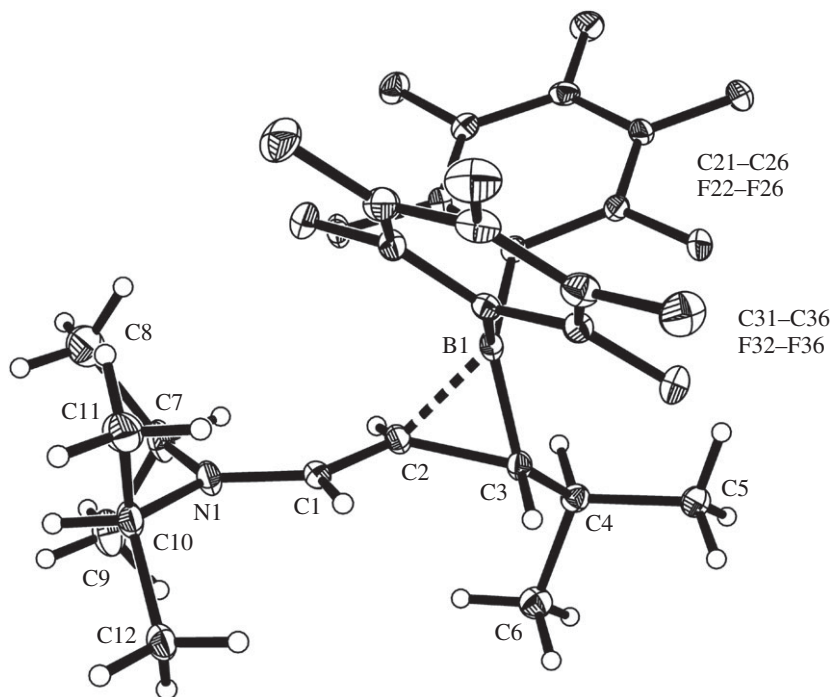


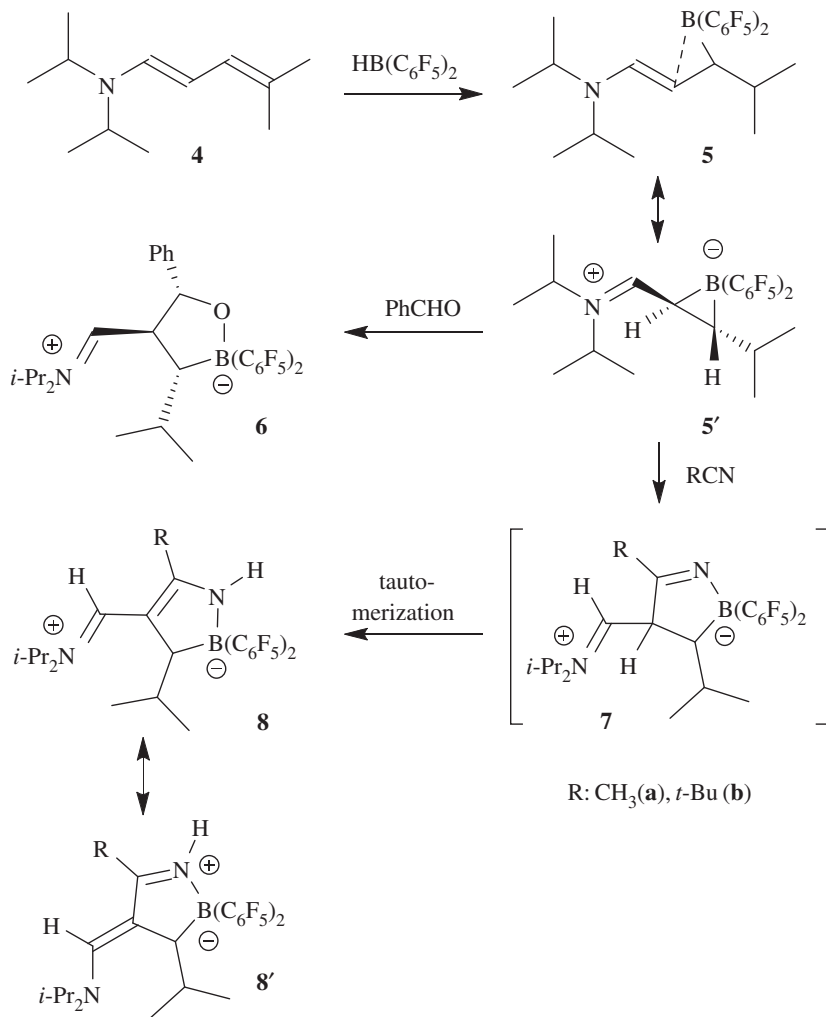
Figure 1. Molecular structure of the dienamine hydroboration product **5/5'** (thermal ellipsoids are shown with 30% probability).

The nuclear magnetic resonance (NMR) spectra of system **5/5'** in d_6 -benzene solution show a ^{11}B NMR feature at $\delta -8.1$, i.e. in the typical tetracoordinated borate range. Consequently, compound **5/5'** shows the ^{19}F NMR resonances of a pair of diastereotopic C_6F_5 substituents at boron with small $\Delta\delta^{19}\text{F}_{\text{m,p}}$ chemical shift differences of 6.4 and 5.6 ppm, respectively. The $i\text{Pr}_2\text{N}=\text{CH}$ -unit shows $^1\text{H}/^{13}\text{C}$ NMR signals at $\delta 6.04/170.3$ and the boratirane $\text{C}2\text{-H}/\text{C}3\text{-H}$ ^1H NMR signals occur at $\delta 2.31/1.87$.

A variety of FLPs undergo 1,2-addition reactions to benzaldehyde and other organic carbonyl compounds [49–51]. Compound **5** reacts analogously. It forms the addition product **6** upon exposure to benzaldehyde at r.t. overnight. We isolated the product after work-up with a 67% yield. The X-ray crystal structure analysis shows that a five-membered heterocycle had been obtained by B–O and C–C bond formation (figure 2). It features the three large substituents in a *trans*-, *trans*-orientation, namely the phenyl group at C13, the iminium cation moiety (N1–C1: 1.291(3) Å) at C2 and the isopropyl group at C3.

Compound **6** shows an iminium type $^1\text{H}/^{13}\text{C}$ NMR pair of signals at $\delta 8.52/184.2$, a ^{11}B NMR feature in the borate anion range ($\delta 2.2$), ^{19}F NMR signals of a pair of diastereotopic C_6F_5 groups at boron as well as six ^1H NMR methyl signals.

The C/B FLP **5/5'** reacts in a similar way with organic nitriles. The reaction with acetonitrile is a typical example. The C/B FLP was prepared *in situ* by treatment of the dienylamine **4** with Piers' borane (pentane, r.t. 2 h) and then acetonitrile was added (approx. 1.1 equiv.) and the reaction mixture stirred overnight at r.t. Work-up gave the product **8a** (R: CH_3) with an approximately 57% yield. We assume that first the primary nitrile addition product **7a** is formed, which then undergoes a tautomerization reaction under the applied reaction conditions. The X-ray crystal structure analysis of **8a** shows the formation of the N-containing five-membered heterocycle (figure 3). It shows the following bond lengths of the conjugated core: N1–C1: 1.338(3) Å, C1–C2: 1.385(3) Å, C2–C13: 1.429(3) Å, and C13–N2: 1.313(3) Å, which indicates a largely delocalized structure of the central N_2C_3 π -system reminiscent of a Zincke-alimine-type derivative [52].



Scheme 2. Preparation of the system **5/5'** and its reactions as a C/B FLP.

Compound **8a/8a'** shows the ¹³C NMR (d₈-toluene, 253 K) feature of the N1–C1 unit at δ 142.2 (¹H: δ 6.58) and of the C13–N2 unit at δ 179.8 (¹H: δ 7.30 NH) and it features the ¹¹B NMR signal at δ –3.1. The C/B FLP **5/5'** reacts similarly with pivalonitrile to give the product **8b**, which shows similar structural and spectroscopic parameters (see the electronic supplementary material for details).

P/B FLPs are known to often typically react with simple binary main group element oxides [53,54]. Therefore, we have exposed our compound **5** to sulfur dioxide in order to find out if it undergoes a related SO₂ C/B FLP addition. Actually, it does (scheme 3). Exposure of the C/B FLP system **5/5'** to SO₂ (1.5 bar) in d₆-benzene gave a full conversion to the C/B FLP SO₂ addition product **9**. Crystals suitable for crystal structure analysis were obtained from a saturated toluene solution layered with pentane at room temperature.

The X-ray crystal structure analysis of the C/B FLP SO₂ addition product **9** shows a central five-membered heterocycle that was formed by addition of the boron Lewis acid to oxygen and the enamine carbon to sulfur (figure 4). It features an envelope-shaped conformation with boron being the tip (angle between the O1–S1–C2–C3/O1–B1–C3 planes: 144.5°). The bond angle at boron amounts to O1–B1–C3 102.1(2)°. The sulfur shows a sum of bond angles of ΣS1^{OOC} 309.8(2)°. In compound **9**, the endocyclic sulfur–oxygen bond length is 1.559(2) Å, whereas the

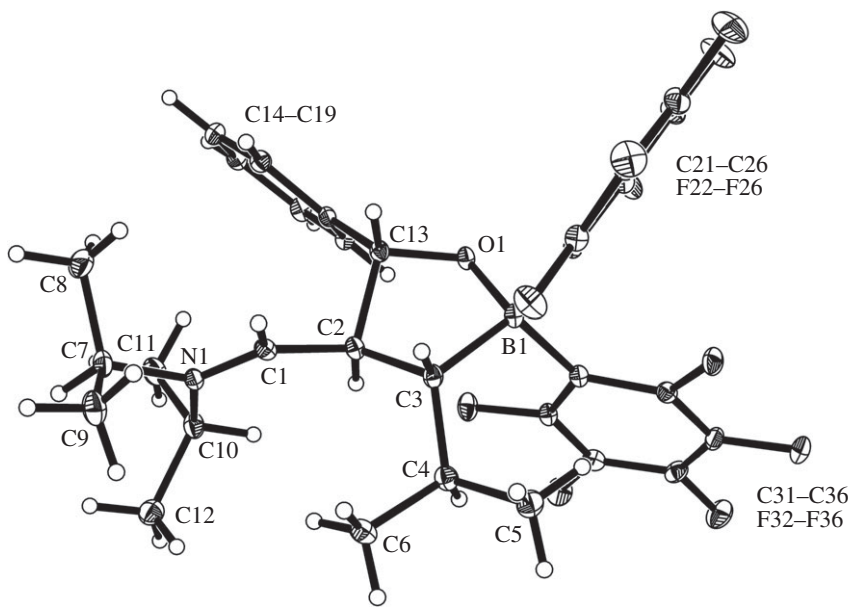


Figure 2. A projection of the molecular structure of the benzaldehyde addition product **6** to the C/B FLP (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (°): O1–C13: 1.402(3), O1–B1: 1.488(3), N1–C1: 1.291(3), C1–C2: 1.462(3), C2–C3: 1.552(3), C2–C13: 1.572(3), C3–B1: 1.674(3), C3–C4: 1.531(4), C13–O1–B1: 109.2(2), C1–N1–C10: 124.1(2), N1–C1–C2: 129.3(2), C3–C2–C13: 101.6(2), C2–C3–B1: 100.6(2).

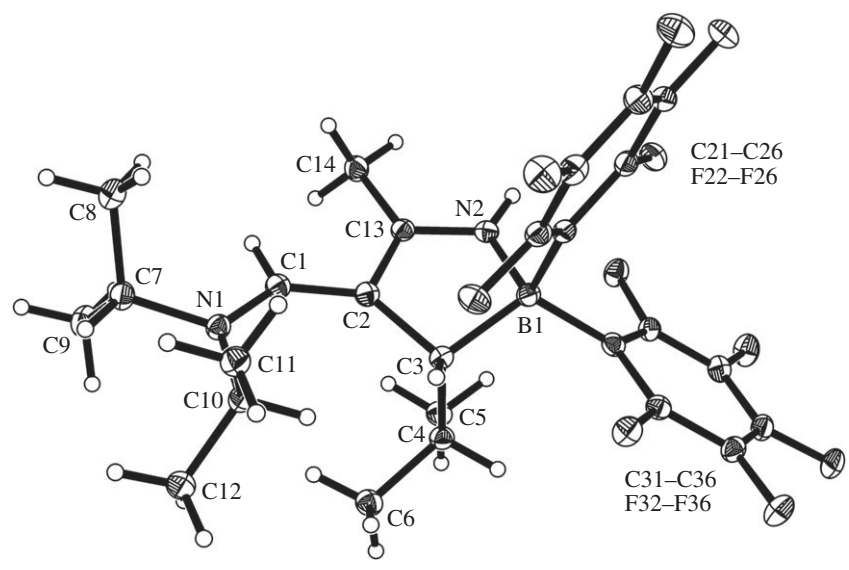
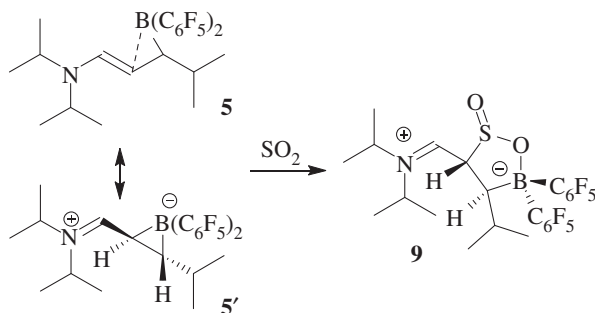


Figure 3. Molecular structure of compound **8a** (thermal ellipsoids are shown with 30% probability).

exocyclic S=O linkage is much shorter at 1.483(2) Å. The newly introduced S=O bond is oriented *cis*-coplanar with the iminium substituent (N1–C1: 1.289(4) Å) at the adjacent carbon atom C2 (θ O2–S1–C2–C1: 11.4(2)°) and it is oriented *trans* to the isopropyl substituent at C3.

In solution (d_6 -benzene), we monitored the NMR signals of a single diastereomer of **9**. It features the ^1H NMR signals of the trio of C1–H/C2–H/C3–H hydrogen atoms at δ 7.69, 4.09



Scheme 3. Reaction of the system 5/5' with SO_2 .

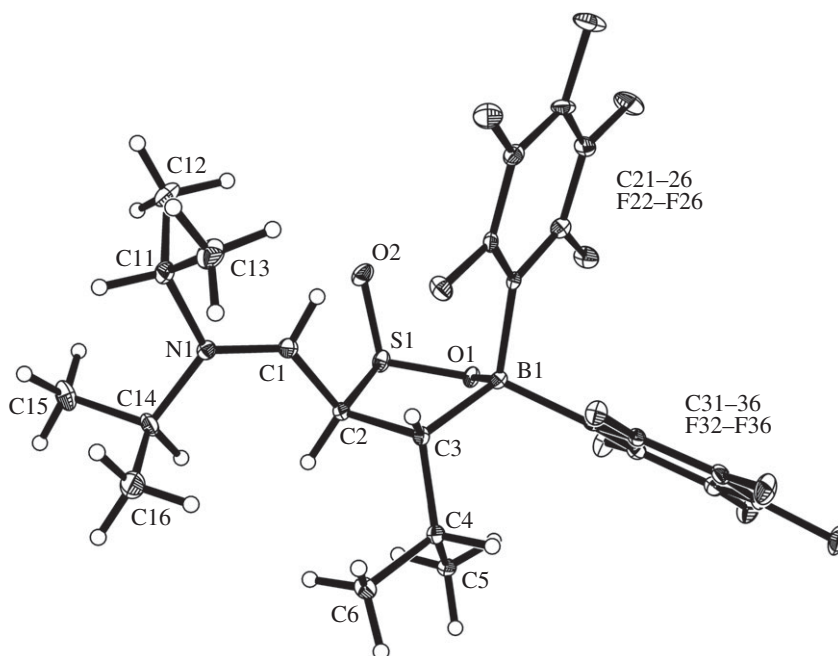


Figure 4. A view of the molecular geometry of the C/B FLP SO_2 adduct **9** (thermal ellipsoids are shown with 30% probability).

and 3.14, in addition to a total of six isopropyl CH_3 doublets and the ^{19}F NMR signals of a pair of diastereotopic C_6F_5 groups at boron (^{11}B NMR: δ 9.3).

We have synthesized the enamine-derived C/B FLP system **5** by a very convenient hydroboration route, namely the reaction of the substituted conjugated dienamine **4** with Piers' borane ($\text{HB}(\text{C}_6\text{F}_5)_2$). The presence of the terminal geminal dimethyl substituents directed the hydroboration reaction completely to form the C3-based borane. Characteristically, the borane Lewis acid forms a weak $\text{C}\cdots\text{B}$ bond with its adjacent enamine-type $\text{C}(\text{sp}^2)$ centre, giving a distorted boratirane structure. This arrangement is similar to a variety of weakly bonded $\text{P}\cdots\text{B}$ or $\text{N}\cdots\text{B}$ situations, and, consequently, our newly formed C/B FLP undergoes typical FLP addition reactions with a variety of added organic π -systems. In the case of the benzaldehyde addition reaction, a stereochemical outcome is obtained that results from a typical minimum steric interaction approach of the PhCHO reagent to the $\text{C}\cdots\text{B}$ boratirane unit. The *trans*-CH-CH arrangement of the latter is also retained to eventually yield the product **6**. In the case of the nitrile addition reactions, the stereochemistry of the C/B FLP addition reaction cannot be

followed due to the rapid subsequent tautomerization process giving rise to the formation of the delocalized nitrogen-containing π -system. Actually, the C/B FLP even adds to SO_2 , giving a typical FLP sulfur dioxide adduct. This study shows that this new type of C/B FLP is easily prepared and shows typical FLP features. We will explore its chemistry further and will see if it helps us to discover new FLP reactions.

Data accessibility. This article has no additional data.

Authors' contributions. B.W. and C.G.D. carried out the X-ray crystal structure analyses.

Competing interests. We declare we have no competing interests.

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