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Frustrated Lewis Pair Chemistry of Chiral (+)-Camphor-Based Aminoboranes

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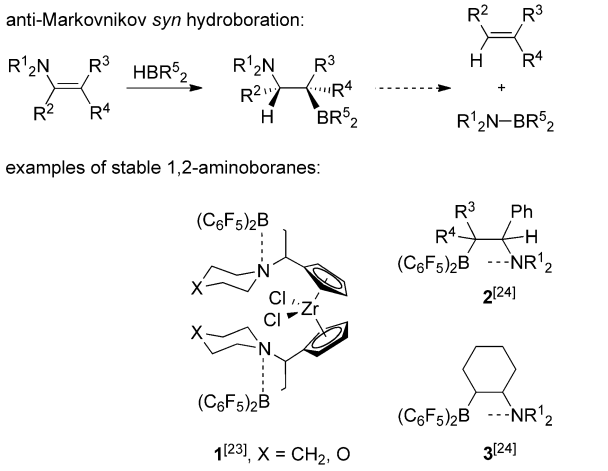
Abstract: Dimethylamino-(+)-camphorenamine reacted with an equimolar amount of Piers' borane, $HB(C_6F_5)_2$, to give the corresponding iminium–hydroborate zwitterionic salt. Being in equilibrium with the parent enamine–$HB(C_6F_5)_2$ N–B pair, this salt was able to split hydrogen heterolytically, hydrogenating the iminium group in the molecule. Detailed studies revealed that the hydrogen splitting in this reaction proceeded through an intermolecular pathway leading to a bornylamine–$HB(C_6F_5)_2$ adduct. When the starting enamine is present in excess over $HB(C_6F_5)_2$, the produced bornylamine–$HB(C_6F_5)_2$ adduct breaks up, eliminating free bornylamine and forming the initial camphorenamine–$HB(C_6F_5)_2$ pair. This results in hydrogenation of the camphorenamine framework in a catalytic fashion.

Keywords: boron · frustrated Lewis pairs · hydrogenation · nitrogen · reaction mechanism

Introduction

Frustrated Lewis pairs (FLP) are combinations of sterically demanding strong Lewis acids and Lewis bases that are not able to form classical adducts.[1] Lewis acidic and basic centers in FLPs have unquenched reactivity that can be used in activation and splitting of small molecules, for example, CO_2,[2] carbonyl compounds,[3] unsaturated hydrocarbons,[4] N_2O,[5] and many others.[6] FLPs are able to split hydrogen heterolytically,[7] opening a way to catalytic hydrogenation of unsaturated organic substrates in the absence of metals.[8] Most of the FLPs studied so far employ substituted boranes and boryl groups as Lewis acidic counterparts.[1,9] From those, $B(C_6F_5)_3$[10] and $HB(C_6F_5)_2$[11] are particularly important. Conversely, Lewis basic centers have been shown to be varied more readily without compromising their reactivity. Among a huge variety of suitable Lewis bases, only phosphines[12] and amines[13] have undeniably displayed the most versatility and usability for hydrogen activation. In addition, splitting of hydrogen has also been performed with FLPs based on Lewis basic carbenes,[14] compounds containing low-valent carbon,[15] or carbonyl groups,[16] among others.[1]

Combinations of bulky amines and $B(C_6F_5)_3$ have been shown to split hydrogen reversibly,[17,18] and it has been demonstrated that combining nitrogen and boron centers in one linked aminoborane system facilitates hydrogen splitting and catalytic hydrogenation reactions.[19] In such *ansa*-aminoboranes, the steric size, basicity and nucleophilicity of the nitrogen counterpart can be tuned in such a way that hydrogen splitting takes place very fast and reversibly so that the ammonium–borate species can catalyze hydrogenations of a large variety of unsaturated substrates, regardless of their steric hindrance.[20] Recently, it has been shown that *o*-aminoborylphenylenes also split hydrogen, even at room temperature.[21] Alternatively, 1,2-aminoboranes with amino and boron centers in neighboring positions can be prepared by selective *syn* hydroboration of enamines. Such N–B systems often decompose, releasing olefins and aminoboranes (Scheme 1).[22] However, Erker and co-workers recently synthesized stable 1,2-aminoboranes from enamines and $HB(C_6F_5)_2$ linked through alkyl or cycloalkyl back-



Scheme 1. Hydroboration of enamines with subsequent deboronation. Examples of stable 1,2-aminoboranes.

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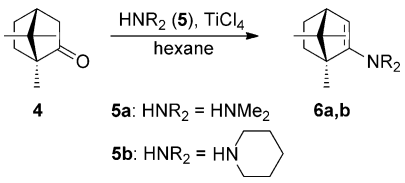
bones.[23,24b] Most of the intramolecular B–N adducts formed were able to activate hydrogen and even worked as catalysts for reduction of enamine substrates. It is proposed that the hydrogen splitting process is thermodynamically permitted in this situation because of release of internal strain caused by formation of a four-membered ring.[21,24b]

Stereoselective (induced by an optically active substrate) *syn* hydroboration of chiral enamines could lead to the respective enantiopure 1,2-aminoboranes. This offers the possibility of metal-free catalytic enantioselective hydrogenation of organic compounds by chiral nitrogen–boron based FLPs.[25] Inspired by these thoughts, we studied reactions between $HB(C_6F_5)_2$ and chiral enamines containing a (1*R*)-(+)-camphor backbone. During the preparation of the present work, Erker and co-workers published parallel studies of a piperidine-substituted (1*R*)-(+)-camphor-1,2-aminoborane,[26] which was found to be in equilibrium between the 1,2-aminoborane and the zwitterionic iminium–hydroborate forms. Our experiments confirm this. Moreover, as shown here, the chemical behavior of these (1*R*)-(+)-camphoraminoboranes can be manipulated by variation of substituents at the nitrogen center. We report herein hydrogen splitting reactions provided by a FLP of dimethyl-(1*R*)-(+)-camphorenamine and Piers' borane, $HB(C_6F_5)_2$.

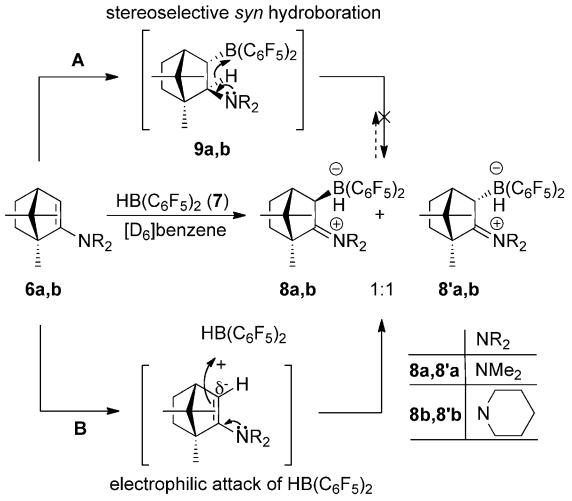
Results and Discussion

Dimethylamino-(1*R*)-(+)-camphorenamine **6a** was obtained by using a procedure reported for its piperidine analogue **6b** by Carlson and Nilsson (Scheme 2).[27] (1*R*)-(+)-Camphor **4** was reacted with dimethylamine **5a** in the presence of $TiCl_4$, and dimethylaminoenamine **6a** was isolated in a good yield from the reaction mixture by distillation under reduced pressure.



Scheme 2. Condensation reaction of (1*R*)-(+)-camphor **4** with amines.

Reaction of enamine **6a** and Piers' borane (**7**; $HB(C_6F_5)_2$) gives the zwitterionic diastereomers **8a** and **8′a** in a 1:1 ratio. Similar behavior was observed by Erker and co-workers for the piperidine analogue **6b** (Scheme 3).[26] The zwitterionic diastereomers **8a** and **8′a** had spectral features that were almost the same as those observed for the **8b**/**8′b** pair. The ^{1}H NMR spectrum of **8a** in [D_6]benzene featured two main series of signals, corresponding to the two formed stereoisomers **8a** and **8′a**. In addition to the ^{1}H NMR signals in the region $\delta_H = 1.4$–3.82 ppm attributed to CH and CH_2 protons of the camphor core (^{1}H NMR, 300 MHz, [D_6]benzene, 27 °C), each stereoisomer produced ^{1}H NMR



Scheme 3. Formation of the zwitterionic iminium–borohydrides **8** and **8′**.

peaks for the diastereotopic methyls of the NMe_2 groups ($\delta_H = 3.56/3.33$ and $3.48/3.03$ ppm) and for the methyl groups of the camphor bridge ($\delta_H = 0.77/0.73$ and $0.94/0.90$ ppm), respectively. The ^{13}C{^{1}H} NMR spectra of **8a** and **8′a** featured signals at $\delta_C = 215.7$ and 216.6 ppm (^{13}C{^{1}H} NMR, 75 MHz, [D_6]benzene, 27 °C), characteristic for iminium carbon atoms (C=NMe_2). Thus, the produced stereoisomers **8a** and **8′a** can be identified as zwitterionic iminium–hydroborates like their piperidine analogues (Scheme 3). The anionic character of the $HB(C_6F_5)_2$ groups in **8a** and **8′a** was elucidated by a characteristic shift of the corresponding ^{11}B NMR signals to a negative region (^{11}B NMR, 160 MHz, [D_6]benzene, 27 °C: $\delta_B = -19.2$ and -22.0 ppm) and typical diastereotopic ^{19}F NMR patterns with $\Delta\delta$(F(*m*,*p*)) values around 3.2 ppm for both isomers. The observed splitting of the ^{11}B NMR signals for **8a** and **8′a** into doublets with typical *J*(B,H) values (96 and 97 Hz, see the Supporting Information for spectral details) indicates that hydrogen remains connected to boron after the reaction. Additional support for the structural identification of the isomers of **8a** and **8′a** was gathered by single-crystal X-ray diffraction studies (Figure 1 and Figure 2).[28] Single crystals suitable for structural analysis were grown by slow evaporation of hexane into a dichloromethane solution of **8** at −30 °C. The obtained crystals contained both diastereomers, **8a** and **8′a**. The salts **8a**/**8′a** feature a camphoriminium core with a hydridoborate group, $HB(C_6F_5)_2^-$, attached to a β-carbon atom (**8a**, C(26)–B(2): 1.698(6) Å; **8′a**, C(1)–B(1): 1.686(6) Å). The distance between the iminium nitrogen and α-carbon atoms is typical for C=N double bonds (**8a**, C(31)–N(36): 1.312(6) Å; **8′a**, C(6)–N(11): 1.302(6) Å).[29] The sum of angles around the α-carbon atom is close to 360°, pointing out its planar configuration and sp^2 character. In diastereoisomers **8a** and **8′a**, the hydridoborate group is oriented either *endo* or *exo*, respectively. Formation of diastereomeric 1:1 mixtures of **8a** and **8′a** excludes a reaction pathway involving stereoselective *syn* hydroboration followed by the

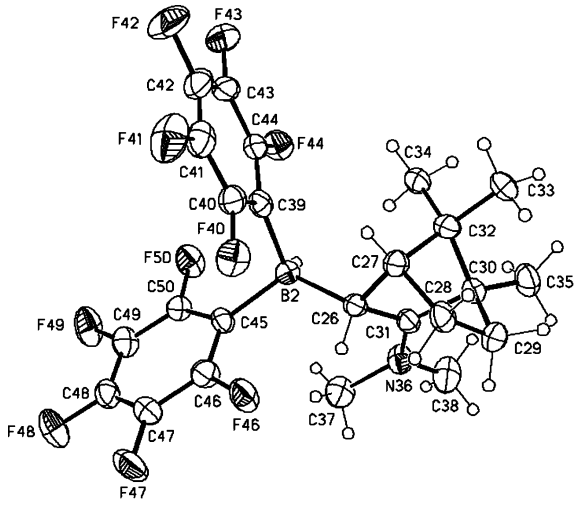


Figure 1. Experimental X-ray structure of **8a**.

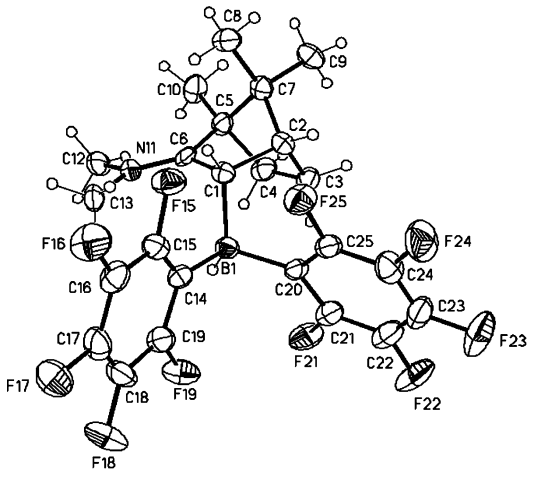
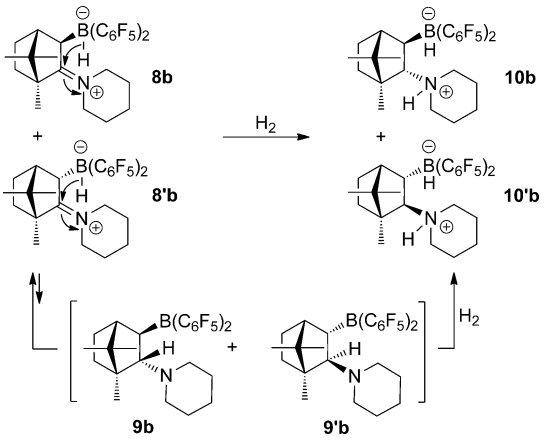


Figure 2. Experimental X-ray structure of **8′a**.

potentially reversible migration of a hydride anion from the C-1 atom back to boron (Scheme 3, path A).[30] Selectivity in the reaction presented in Scheme 3 is lost due to the fact that it is not a concerted *syn* hydroboration but, rather, an electrophilic attack by $HB(C_6F_5)_2$ to the polarized enamine double bond. Electrophilic addition to 1-aminocyclohexenes places a new substituent in an axial orientation favoring the chair intermediate over the twist boat conformation.[31] The camphor bridge locks the conformation of the cyclohexene ring into the boat form, leading to the loss of selectivity. Thus, electrophilic attack proceeds either from above or below to the electron-rich p orbital on the C2-carbon (Scheme 3, path B).

In addition to the iminium–borohydrides **8a** and **8′a**, the NMR spectra revealed signals belonging to a minor product. Even though the presence of the parent aminoborane **9a** (Scheme 3) was expected, conversely, these data corresponded to the B–N adduct of enamine **6a** and $HB(C_6F_5)_2$. This minor component of the system featured in the ^{11}B NMR spectrum as a signal at $\delta_B = -8.5$ ppm (^{11}B NMR, 160 MHz, [D$_6$]benzene, 50 °C), characteristic for B–N adducts. Additionally, ^1H NMR resonances corresponding to the C=C double bond proton at $\delta_H = 6.02$ ppm (vs. $\delta_H = 4.77$ ppm for the parent enamine **6a**) and for the NMe_2 groups at $\delta_H = 3.00$ ppm (^1H NMR, 300 MHz, [D$_6$]benzene, 27 °C) were observed. Unfortunately, ^1H NMR signals of the camphor protons could not be distinguished from those displayed by the major components of the system, the iminium–borohydrides **8a** and **8′a**. In addition to ^{19}F NMR signals for the iminium–borohydrides **8a** and **8′a**, ^{19}F NMR peaks corresponding to the **6a**–$HB(C_6F_5)_2$ adduct were found at $\delta(F_o) = -128.8$, -129.2 ppm, $\delta(F_p) = -157.4$, -158.3 ppm and $\delta(F_m) = -164.0$, -164.4 ppm (^{19}F NMR, 282 MHz, $CDCl_3$, 27 °C). By performing variable-temperature ^1H NMR and ^{19}F NMR experiments in [D$_8$]toluene, we were able to shift the equilibrium between the **6a**–$HB(C_6F_5)_2$ adduct and the iminium–borohydrides **8a** and **8′a** from a ratio of 1:8 at 27 °C to 1:5 at 75 °C.

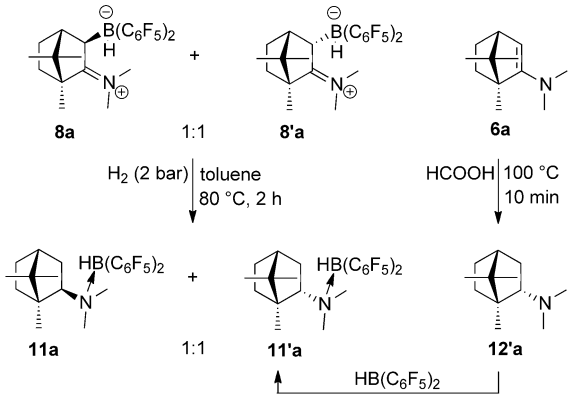
The diastereomeric pair **8b** and **8′b** splits hydrogen through intermediate formation of 1,2-aminoboranes **9b** and **9′b**, leading to the hydrogenated ammonium–borohydride diastereomers **10b** and **10′b** (Scheme 4).[26] Surprisingly, the



Scheme 4. Formation of the zwitterionic ammonium–hydroborates **10b** and **10′b**.[26]

dimethyliminium–hydroborates **8a** and **8′a** reacted with hydrogen in a different way to the recently described piperidinium analogues **8b** and **8′b**.

Conversely, upon stirring the **8a**/**8′a** mixture for 2 h in toluene at 80 °C under an atmosphere of hydrogen (2 atm), adducts of *N*,*N*-dimethylisobornylamine and *N*,*N*-dimethylbornylamine with $HB(C_6F_5)_2$ (**11a** and **11′a**, respectively) were obtained in a 1:1 ratio (Scheme 5). In their ^{11}B NMR spectrum, compounds **11a** and **11′a** display a broad signal at $\delta_B = -7.8$ ppm (^{11}B NMR, 160 MHz, $CDCl_3$, 27 °C), which is characteristic for boron–nitrogen adducts (see the Supporting Information for further details). ^1H NMR signals of the CH protons at the C-1 carbon atoms are shifted downfield: $\delta_H = 3.59$ (**11a**) and 3.79 (**11′a**) ppm. To confirm the assigned



Scheme 5. Hydrogen splitting by iminium–hydroborates **8a**/**8′a**.

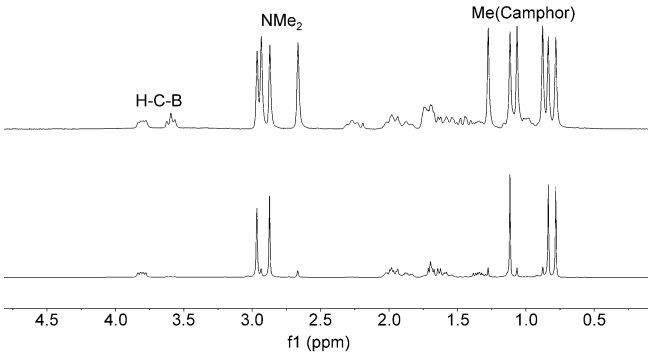
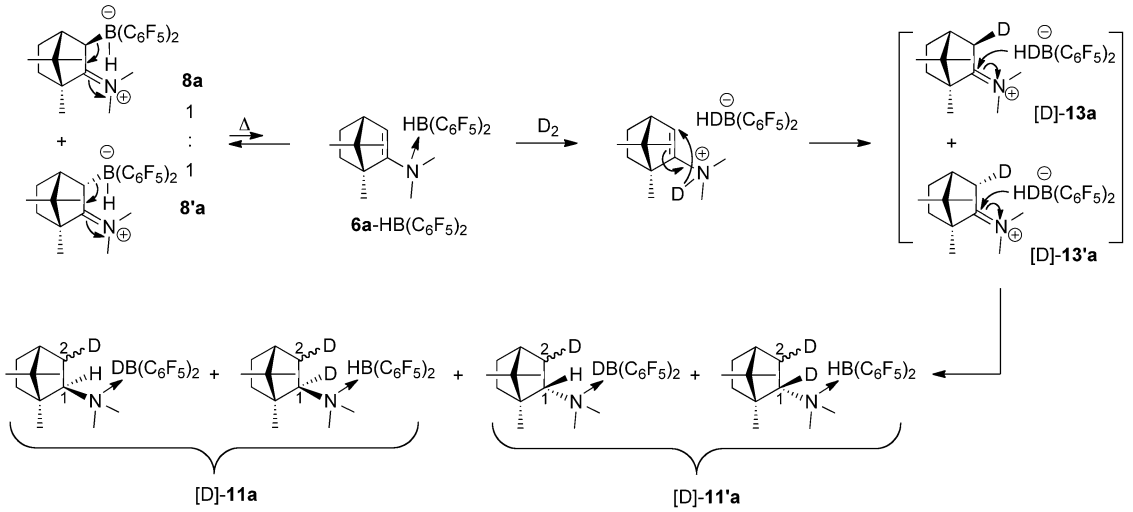


Figure 3. ^{1}H NMR spectra (300 MHz, $CDCl_3$, 27 °C) of hydrogen splitting products obtained from **8a**/**8′a** (top) and adduct **11′a** (bottom), synthesized by mixing amine **12′a** and $HB(C_6F_5)_2$.

structures, adduct **11′a** was synthesized in an alternative way. Enamine **6a** was hydrogenated by heating with formic acid.[27] This reaction gave bornylamine **12′a** selectively. Treatment of **12′a** with $HB(C_6F_5)_2$ led to the *endo* isomer **11′a** (Scheme 5). This product has exactly the same NMR spectral characteristics as those obtained independently from hydrogen splitting reactions (Figure 3).

To determine the internal process involved in the hydrogen splitting reaction, we studied splitting of deuterium with the **8a**/**8′a** pair (conditions: toluene, 2 atm of deuterium, 2 h at 80 °C). This reaction led to the corresponding deuterated *exo*/*endo* adducts [D]-**11a** and [D]-**11′a** (Scheme 6). Stereoisomers [D]-**11** featured ^{2}H NMR signals of *exo*/*endo* deuterium atoms connected to the C-1 and to C-2 carbon atoms of the bornyl/isobornyl core (^{2}H NMR, 77 MHz, $CDCl_3$, 27 °C: $\delta_D = 3.64$, 3.35 and 1.90–1.33 ppm, respectively).

The products [D]-**11** also displayed ^{1}H NMR signals of *exo*/*endo* hydrogen atoms bound to C-1 carbon atoms (^{1}H NMR, 300 MHz, $CDCl_3$, 27 °C: $\delta_H = 3.64$ and 3.35 ppm). The total integration of intensity of these signals was only 50 %, in comparison to the otherwise identical spectrum of the hydrogen splitting products, **11a** and **11′a**, being a result of H^- or D^- attack with an equal probability in the species [D]-**13a** and [D]-**13′a** (Scheme 6).[32] The ^{13}C{^{1}H} NMR signals of the C-2 carbon atoms in [D]-**11a** and [D]-**11′a** were recorded as a combination of several triplets at $\delta_C = 31.3$ and 34.4 ppm (^{13}C{^{1}H} NMR,126 MHz, $CDCl_3$, 27 °C), which is characteristic for monodeuterated −CHD− groups.[33] The deuterated C-1 carbon atom gave low intensity triplets at $\delta_C = 76.1$ and 72.4 ppm, whereas sharp singlets at $\delta_C = 76.4$ and 72.9 ppm were attributed to the protonated C-1 carbon atoms (see spectral details in the Supporting Information). These results indicated that hydrogen splitting reactions with isomers **8a** and **8′a** and their piperidinium analogues **8b** and **8′b** occurred through different reaction pathways. Whereas piperidine-derived iminium–hydroborates **8b** and **8′b** gave the corresponding ammonium–hydroborate products **10b** and **10′b** (Scheme 4), their dimethyliminium analogues **8a** and **8′a** transformed into amino–borane adducts **11a** and **11′a**. As shown by Erker et al.,[26] the former reaction proceeded through an intermediate rearrangement of **8b** and **8′b** salts into the corresponding aminoboranes **9b**



Scheme 6. Deuterium splitting with the system **8a**/**8′a**.

and **9′b** that were responsible for hydrogen splitting (Scheme 4). In our case, it seems that splitting of hydrogen takes place through the **6a**–$HB(C_6F_5)_2$ N–B adduct. It has been observed that the zwitterionic system **8a** and **8′a** is in equilibrium with **6a**–$HB(C_6F_5)_2$, which is a minor component in solution (see above). This situation changes remarkably in the presence of hydrogen. Despite its coordinative nature, **6a**–$HB(C_6F_5)_2$ might behave as an active FLP and split hydrogen or deuterium (Scheme 6). This should move the reaction equilibrium from the zwitterionic form **8a** and **8′a** to the side of the **6a**–$HB(C_6F_5)_2$ adduct and then further towards **11a** and **11′a** products (for the deuterium case [D]-**11a** and [D]-**11′a**, respectively). In the proposed sequence (Scheme 6), addition of the $[HDB(C_6F_5)_2]^-$ anion to the iminium cation in the intermediately formed [D]-**13** salts should lead to [D]-**11a** and [D]-**11′a** isomers, for which the C-1 carbon atoms should be connected with an equal probability either with deuterium or hydrogen.[32] All these [D]-**11a** and [D]-**11′a** products, deuterated and hydrogenated at the C-1 carbon atoms, were detected in NMR studies (see above).

Starting from the unsaturated camphor framework **6a**, hydrogen splitting reactions with zwitterionic salts **8a** and **8′a** led to the fully hydrogenated *N*,*N*-dimethylbornyl- and isobornylamines. This process could also be carried out in a catalytic fashion.[24] By adding 10 mol% $HB(C_6F_5)_2$ to **6a** and heating the resulting mixture in [D_6]benzene at 80 °C for 16 h under 2 atm H_2, enamine **6a** was hydrogenated (with 98% conversion verified by NMR spectroscopic analysis) into the corresponding *N*,*N*-dimethylbornyl- and isobornylamines (with a bornyl- and isobornyldimethylamine ratio of 1:2). Quite surprisingly, this hydrogenation reaction produced isobornyldimethylamine as a major product, in contrast to reduction with formic acid for which it was obtained in a negligible amount. As a result of hydrogenation, an amine–borane adduct **11a**/**11′a** is formed that reacts with an excess of the starting enamine **6a** giving the initial iminium–borohydride system **8a** and **8′a**, which keeps the hydrogenation process running in a catalytic mode.[8d,20] It was observed that at 27 °C in a 1:1:1 mixture of isobornylamine **12′a**, enamine **6a**, and $HB(C_6F_5)_2$, only 60% of total $HB(C_6F_5)_2$ amount was bound to amine **12′a** and the rest reacted with **6a** to give zwitterionic salts **8a** and **8′a**, 2% of which was present in the form of the **6a**–$HB(C_6F_5)_2$ adduct. These results suggest applicability for catalytic hydrogenation of enamines with Piers' borane when equilibrium between the resulting amine and the starting enamine–borane adduct is achieved.

Conclusion

Dimethylcamphorenamine **6a** was prepared and reacted with $HB(C_6F_5)_2$ to give stable respective iminium–hydroborate zwitterionic salts **8a**/**8′a**. Surprisingly, the products were able to split hydrogen heterolytically. Variable-temperature NMR experiments show that, in solution, the iminium–hydroborate form is, in fact, in equilibrium with the adduct of the starting enamine **6a** and $HB(C_6F_5)_2$. This minor component of the equilibrium, **6a**–$HB(C_6F_5)_2$ adduct, behave at elevated temperatures as an active FLP, performing splitting of hydrogen and in this way moving the equilibrium from the iminium–hydridoborate side to that of the hydrogenated products. The size of the nitrogen substituent in the camphor-based aminoboranes has a remarkable influence on the structure of the equilibrium products and, consequently, on the result of the hydrogen splitting process. In the presence of hydrogen, bulky piperidine groups stabilize the 1,2-aminoborane framework against the dehydroboration process. As a result, piperidine derivatives were hydrogenated into the corresponding camphor-linked ammonium–hydroborates. Conversely, small methyl substituents facilitate intermediate formation of an adduct between the starting camphorenamine and $HB(C_6F_5)_2$ borane, thus providing an active intermolecular frustrated Lewis pair, which is responsible for splitting of hydrogen and formation of bornylamines as products of hydrogenation.

Experimental Section

General: All experiments were performed either by using a dual-manifold gas-inlet/vacuum line or in a glove box (MBraun Unilab) under an argon atmosphere. H_2 was purchased from Oy AGA Ab as Scientific Hydrogen 6.0 grade and used without further purification. All reagents were purchased from Sigma–Aldrich or Strem and purified by conventional methods. Solvents were dried according to published procedures and distilled under an argon atmosphere. NMR experiments were performed with a Varian Mercury 300 MHz spectrometer.

1-(1,7,7-Trimethylbicyclo[2.2.1]hept-2-en-2-yl)dimethylamine (6a): A solution of $TiCl_4$ (3.6 mL, 33 mmol) in hexane (10 mL) was added dropwise at −30 °C to a solution of dimethylamine (14 mL, 207 mmol) in hexane (25 mL). Subsequently, a solution of (+)-camphor (3.7 g, 25 mmol) in hexane (15 mL) was added at such a rate that the reaction mixture did not reach reflux. The reaction mixture was stirred overnight at 25 °C, then the resulting suspension was filtered twice through a sintered glass filter (porosity grade 4 and 3). The filtered clear solution was collected and the remaining volatiles were removed under reduced pressure. The product was isolated by distillation under vacuum (b.p. 46 °C/3 mmHg) as a colorless oil (3.3 g, 18.2 mol, 72%). ^{1}H NMR (300 MHz, $CDCl_3$, 27 °C): δ = 4.77 (d, J = 3.6 Hz, 1H; =CH), 2.48 (s, 6H; $N(CH_3)_2$), 2.18 (m, 1H; CH), 1.83 (ddt, J = 11.2, 9.0, 3.5 Hz, 1H; CH), 1.50 (ddd, J = 12.0, 8.9, 3.5 Hz, 1H; CH_2), 1.15 (m, 1H; CH_2), 1.01 (m, 1H; CH_2), 1.09, 0.84, 0.72 ppm (each s, each 3H, CH_3); ^{13}C{H} NMR (75 MHz, $CDCl_3$, 27 °C): δ = 159.6, 108.0, 56.8, 54.0, 50.0, 42.6, 32.3, 27.5, 20.3, 20.1, 12.7 ppm.

Iminium–borohydrides 8a and 8′a: $HB(C_6F_5)_2$ (35 mg, 0.1 mmol) was dissolved in [D_6]benzene and enamine **6a** (18 mg, 0.1 mmol) was added to the solution at RT. The suspension was stirred for approximately 5 min, during which all solids dissolved. Quantitative conversion was verified by ^{1}H and ^{19}F NMR spectroscopy. Crystals were grown by slow evaporation of hexane into a dichloromethane solution. Elemental analysis calcd (%) for $C_{27}H_{26}BF_{10}N$: C 54.88, H 4.22, N 2.67; found C 54.82, H 4.24, N 2.67.

Compound 8a: ^{1}H NMR (300 MHz, $CDCl_3$, 27 °C): δ = 3.56 (s, 3H; NCH_3), 3.33 (s, 3H; NCH_3), 3.25–2.25 (br m, 1H; BH), 3.15 (br s, 1H; CH), 2.04 (m, 3H; CH), 1.96 (m, 1H; CH_2), 1.85 (m, 1H; CH_2), 1.45 (m, 1H; CH_2), 1.36 (m, 1H; CH_2), 1.37 (s, 3H; CH_3), 0.77 (s, 3H; CH_3), 0.73 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 27 °C): δ = 215.71, 149.8, 146.6, 138.7, 135.4, 61.4, 51.5, 50.9, 50.0, 48.4, 44.1, 33.9, 30.1, 22.2, 20.2, 15.1 ppm.

Compound 8′a: ^{1}H NMR (300 MHz, $CDCl_3$, 27 °C): δ = 3.80 (br s, 1H; CH), 3.48 (s, 3H; NCH_3), 3.25–2.25 (br m, 1H; BH), 3.03 (s, 3H; NCH_3), 2.00 (m, 1H; CH), 1.93 (m, 1H; CH_2), 1.75 (m, 1H; CH_2), 1.74 (m, 1H; CH_2), 1.50 (m, 1H; CH_2), 1.28 (s, 3H; CH_3), 0.94 (s, 3H; CH_3), 0.90 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 27 °C): δ = 216.7, 149.8, 146.6, 138.7, 135.4, 61.4, 56.2, 49.8, 46.8, 46.3, 44.7, 31.4, 23.4, 20.4, 19.4, 15.9 ppm.

Compound 8a/8′a: ^{19}F NMR (282 MHz, $CDCl_3$, 27 °C): δ = −130.3 (m, 2F; *o*-$C_6F_5^A$), −132.2 (m, 2F; *o*-$C_6F_5^B$), −132.5 (m, 2F; *o*-$C_6F_5^C$), −133.0 (br s, 2F; *o*-$C_6F_5^D$), −161.5 (t, J = 20.3 Hz, 1F; *p*-$C_6F_5^A$), −161.6 (t, J = 20.4 Hz, 1F; *p*-$C_6F_5^C$), −162.3 (t, J = 20.4 Hz, 1F; *p*-$C_6F_5^D$), −162.4 (t, J = 20.2 Hz, 1F; *p*-$C_6F_5^B$), −164.9 (m, 2F; *m*-$C_6F_5^C$), −165.3 (m, 2F; *m*-$C_6F_5^D$), −165.4 (m, 2F; *m*-$C_6F_5^A$), −165.6 ppm (m, 2F; *m*-$C_6F_5^B$); ^{11}B NMR (160 MHz, [D$_6$]benzene, 50 °C): δ = −19.2 (d, J = 97.1 Hz), −22.0 (d, J = 95.7 Hz).

***N,N*-Dimethylbornyl-/isobornylamine–HB(C_6F_5)$_2$ adducts 11a and 11′a**: A 25 mL Schlenk tube with a magnetic stirring bar, containing the in situ formed iminium-borohydride **8a/8′a** (0.4 mmol) in toluene (2 mL) was pressurized to 2 atm with dihydrogen. The solution was stirred (1000 rpm) at 80 °C for 2 h. The solvent was removed under reduced pressure, leaving a sticky solid, which was further washed with hexane. The white precipitation was collected and dried under vacuum. Yield: 180 mg (0.34 mmol, 85 %). Elemental analysis calcd (%) for $C_{27}H_{28}BF_{10}N$: C 54.67, H 4.59, N 2.66; found C 54.24, H 4.27, N 2.67.

Compound 11a: ^{1}H NMR (300 MHz, [D$_6$]benzene, 27 °C): δ = 4.25–2.02 (br m, 1H; BH), 3.37 (t, J = 9.0 Hz, 1H; CH), 2.37 (s, 3H; CH_3), 2.07 (s, 3H; CH_3), 1.77 (m, 1H; CH_2), 1.32 (m, 1H; CH_2), 1.28 (m, 1H; CH_2), 1.14 (m, 1H; CH_2), 1.11 (m, 1H; CH_2), 0.80 (m, 1H; CH_2), 0.77 (s, 3H; CH_3), 0.65 (m, 1H; CH_2), 0.57 (s, 3H; CH_3), 0.50 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 27 °C): δ = 150.4, 147.2, 141.8, 139.3, 138.7, 136.3, 76.5, 51.9, 51.2, 48.1, 47.4, 43.2, 41.9, 34.7, 26.2, 22.0, 21.5, 15.4 ppm.

Compound 11′a: ^{1}H NMR (300 MHz, [D$_6$]benzene, 27 °C): δ = 4.25–2.02 (br m, 1H; BH), 3.63 (dd, J = 10.6, 5.7 Hz, 1H; CH), 2.40 (s, 3H; CH_3), 2.23 (s, 3H; CH_3), 1.70 (m, 1H; CH_2), 1.47 (m, 1H; CH_2), 1.35 (m, 1H; CH_2), 1.24 (m, 1H; CH_2), 1.19 (m, 1H; CH_2), 1.10 (m, 1H; CH_2), 0.83 (m, 1H; CH_2), 0.72 (s, 3H; CH_3), 0.54 (s, 3H; CH_3), 0.52 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 27 °C): δ = 150.4, 147.2, 141.8, 139.3, 138.7, 136.3, 72.9, 51.9, 51.4, 48.1, 45.5, 43.2, 31.7, 28.8, 27.5, 22.0, 18.2, 17.5 ppm.

Compound 11a/11′a: ^{19}F NMR (282 MHz, [D$_6$]benzene, 27 °C): δ = −128.3 (m, 2F; *o*-$C_6F_5^A$), −128.6 (m, 2F; *o*-$C_6F_5^B$), −128.6 (m, 2F; *o*-$C_6F_5^C$), −128.6 (m, 2F; *o*-$C_6F_5^D$), −156.6 (t, J = 20.7 Hz, 1F; *p*-$C_6F_5^B$), −157.0 (t, J = 20.7 Hz, 1F; *p*-$C_6F_5^C$), −157.6 (t, J = 20.7 Hz, 1F; *p*-$C_6F_5^D$), −158.1 (t, J = 20.7 Hz, 1F; *p*-$C_6F_5^A$), −163.7 (m, 2F; *m*-$C_6F_5^B$), −163.8 (m, 2F; *m*-$C_6F_5^C$), −163.9 (m, 2F; *m*-$C_6F_5^D$), −164.0 ppm (m, 2F; *m*-$C_6F_5^A$); ^{11}B NMR (160 MHz, [D$_6$]benzene, 50 °C): δ = −7.91 ppm.

Bornyldimethylamine (12′a): Enamine **7a** (360 mg, 2 mmol) was heated under an argon atmosphere to 100 °C. Formic acid (0.15 mL, 4 mmol) was added at such a rate that foaming was kept under control. After addition, the reaction mixture was heated for 10 min at 100 °C. 1 M HCl (10 mL) was added and the aqueous phase was extracted with diethyl ether (2 × 10 mL). The aqueous phase was collected and basified with 1 M NaOH, giving a milky emulsion, which was further extracted with diethyl ether (3 × 10 mL). The organic phase was dried and all volatiles were removed, leaving the product as a yellow oil (252 mg, 1.39 mmol, 70 %). ^{1}H NMR (300 MHz, $CDCl_3$, 27 °C): δ = 2.21 (s, 6H; $N(CH_3)_2$), 2.05 (m, 1H; NCH), 2.05 (m, 1H; CH_2), 1.90 (m, 1H; CH_2), 1.72 (m, 1H, CH_2), 1.55 (m, 1H; CH), 1.28 (m, 2H; CH_2), 1.05 (m, 1H; CH_2), 0.96, 0.87, 0.82 ppm (each s, each 3H; CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 27 °C): δ = 72.8, 50.4, 48.5, 46.4, 44.5, 38.4, 29.0, 27.4, 20.4, 18.9, 17.0 ppm.

Catalytic hydrogenation of enamine 6a: A 25 mL Schlenk tube with a magnetic stirring bar, containing a solution of enamine **6a** (180 mg, 1 mmol) and HB(C_6F_5)$_2$ (35 mg, 0.1 mmol) in [D$_6$]benzene (1 mL) was pressurized to 2 atm H_2. The solution was stirred (1000 rpm) at 80 °C for 16 h, then cooled and transferred to an NMR tube. Conversion was 98 % (determined by ^{1}H NMR spectroscopic analysis). Ratio of bornyl and isobornyl dimethylamines was 1:2.

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