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Reversible hydrogen activation by a bulky haloborane based FLP system

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The FLP species bis(2-(TMP)phenyl)chloroborane (TMP=2,2,6,6-tetramethylpiperidine)(**1**) was prepared and crystallized as a monomeric Frustrated Lewis Pair (FLP) displaying no apparent B-N interaction. Species **1** readily reacts with H_2 at room temperature to generate reversibly the zwitterionic H_2 activation product **2**. Interestingly, in the presence of a base, **2** releases HCl, generating the novel FLP species **3** which is also monomeric.

Introduction

The initial discovery of Frustrated Lewis Pairs (FLPs) by Welch, Stephan and co-workers[1] paved the path to a decade of rich and diverse metal-free chemistry.[2–6] While the original reports were limited to the stoichiometric activation of small molecules,[7–14] FLPs quickly emerged as potent hydrogenation catalysts for polar substrates.[15–19] It was not long before novel ambiphilic systems were shown to promote a wide variety of catalytic transformations,[20] some reaching activities rivaling with that of transition-metal based systems.[21–30]

Amine-borane based FLPS have proven to be very versatile, allowing a number of unprecedented catalytic transformations. The first N/B system(Figure 1, **A**) was reported as early as 2003 by Piers and Roesler.[31] Unfortunately, due to the limited Lewis basicity of the diphenylamino substituent, the original molecule did not generate a stable zwitterionic H_2 splitting product. Perhaps the most interesting part of the report is the conclusion when authors mentioned that *''the basicity of the nitrogen center in an aminoborane would have to be significantly higher in order to thermodynamically favor the formation of a dihydrogen adduct…''*. Indeed, this conclusion was confirmed almost a decade later by Repo and co-workers who managed to activate H_2 by simply substituting the phenyl groups on nitrogen for methyl or TMP moieties (Figure 1, **B** and **C**, respectively; TMP = 2,2,6,6-tetramethylpiperidine).[32,33]

The first example of an amine-based FLP system for H_2 splitting ($TMP/B(C_6F_5)_3$) was also reported by Repo, as early as 2008.[34] By incorporating the active centers in an intramolecular framework (Figure 1, **D**), the authors were able to effect catalytic hydrogenation, demonstrating the potential of this type of FLP systems.[33] Pushing the concept further, an asymmetric version of these molecular tweezers (Figure 1, **E**) was prepared.[35] Very recently, an improved version of the catalyst (Figure 1, **F**) was reported to achieve remarkable selectivities, up to 99% ee.[36] It should also be noted that Du and co-workers were able to exploit the N/B pairing to develop an intermolecular strategy for asymmetric hydrogenations.[37–39]

Another major breakthrough in the field of FLP chemistry originated from aminoborane **B** (Figure 1) that was shown to promote the catalytic hydrogenation of alkynes through an unprecedented mechanism.[40] While Ashley and O'Hare reported that the $TMP/B(C_6F_5)_3$ tandem can hydrogenate CO_2 to methanol under forcing conditions,[41] a recent collaboration with the group of Stephan allowed us to demonstrate that **G** (Figure 1) allows the room temperature hydrogenation of CO_2.[42] A robust N/B FLP based on this framework was also reported (Figure 1, **H**).[43]

Most recently, we have described that FLP **I** (Figure 1), which was also reported by Repo *et al.* to cleave the dihydrogen molecule reversibly,[44] was capable of effecting the catalytic borylation of electron-rich heteroarenes, demonstrating for the first time that FLPs could act as catalysts for the direct functionalization of Csp^2 -H bonds.[30]

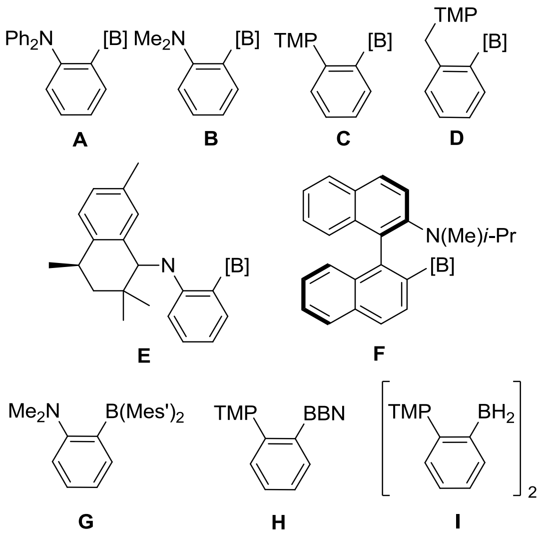

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Figure 1: Reported intramolecular N/B FLPs. [B]= $B(C_6F_5)_2$, BBN=9-Borabicyclo[3.3.1]nonane, Mes'=2,4,5-$Me_3C_6H_2$

The richness of transformations mediated by N-B FLPs has prompted us investigate these architectures. Herein, we have successfully prepared compound **1** which bears two Lewis basic TMP moieties, contrasting with the typical single-base/single-acid FLP framework. Examples of ambiphilic molecules composed of multiple Lewis basic sites have only appeared sporadically in the literature[45–51] and have been scarcely studied for FLP applications.[21] The new compound is also a rare example of an FLP system bearing an halogen atom directly at the boron center.[52,53] Herein, the preparation and reactivity of this unusual FLP system are reported.

Experimental section

General experimental

Unless specified otherwise, manipulations were carried out under a nitrogen atmosphere using standard glovebox and Schlenk techniques. Hexanes, toluene and tetrahydrofuran (THF) were purified by distillation over Na/benzophenone. Benzene-*d₆* was dried over Na/K alloy and distilled. NMR spectra were recorded on an Agilent Technologies NMR spectrometer at 500 MHz (^1H), 125.758 MHz (^{13}C), 160.46 MHz (^{11}B) and on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^1H), 100.580 MHz (^{13}C). ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are referenced to residual protons or carbons in deuterated solvent. $^{11}B\{^1H\}$ was calibrated using an external reference of $BF_3.Et_2O$. Multiplicities are reported as singlet (s), broad singlet (s, br) doublet (d), triplet (t), multiplet (m). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. [2-(2,2,6,6-tetramethylpiperidin-1-yl)phenyl]lithium was prepared according to a known literature procedure.[32] $LiAlH_4$ and TMSBr were purchased from Sigma-Aldrich and used as received. Elemental analyses were performed with a Thermo Scientific Flash 2000 CHNS Analyser. All the attempts to analyze the new compounds reported by mass spectroscopy failed and only hydrolysis products were observed.

Computational details

All the calculations were performed on the full structures of the reported compounds. Calculations were performed with the Gaussian 09 suite of programs. The ω-B97XD functional[54] was qualified as promising by Grimme[55] and was previously used to accurately describe the mechanism of FLP mediated transformations[30,40] and was thus used in combination with the 6-31G** basis set for all atoms.[56,57] The transition states were located and confirmed by frequency calculations (single imaginary frequency). The stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency). All geometry optimizations were carried out without any symmetry constraints. The energies were then refined by single point calculations to include solvent effects using the SMD solvation model[58] with the experimental solvent (benzene) at the ω-B97XD /6-31+G** level of theory. All structures with their associated free enthalpy and Gibbs free energies as well as their Cartesian coordinates are fully detailed in the supporting information. Free energies are reported as follows: ΔG (ΔH) in $kcal.mol^{-1}$.

Crystallographic details:

Crystals were mounted on CryoLoops with Paratone-N and optically aligned on a Bruker SMART APEX-II X-ray diffractometer with 1K CCD detector using a digital camera. Initial intensity measurements were performed using a fine-focused sealed tube, graphite-monochromated, X-ray source (Mo *Kα*, λ = 0.71073 Å) at 50 kV and 30 mA. Standard APEX-II software package was used for determining the unit cells, generating the data collection strategy, and controlling data collection. SAINT[59] was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using SCALE (SADABS[60]). The structures of all compounds were solved by direct methods and refined by full-matrix least-squares methods with SHELX-97[61] in the SHELXTL6.14 package. All of the H atoms on C atoms were generated geometrically and refined in riding mode. Crystallographic information for all obtained phases is summarized in Table S1. Atomic coordinates and additional structural information are provided in the .cif files of the Supporting Information. Crystallographic data have been deposited with CCDC (CCDC No. 1429583 (**1**), 1429582 (**2**), 1429581 (**3**)). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk, or via the Internet at www.ccdc.cam.ac.uk.

Synthesis of compounds:

bis(2-(TMP)phenyl)chloroborane (1) ***:*** 1.80 g (8.06 mmol, 2 equiv)) of [2-(2,2,6,6-tetramethylpiperidin-1-yl)phenyl]lithium] were placed in a Schlenk flask along with a teflon coated stirring bar inside the glovebox. Then *ca* 40 mL of hexanes were added to the solid and the resulting slurry was stirred vigorously and cooled down to -78 °C. 4.0 mL of a 1M solution of BCl_3 (4.0 mmol) in hexanes was added at once and the cold bath was removed, leaving the reaction mixture to warm to room temperature naturally. The reaction was left stirring overnight, giving a bright yellow solution with a white precipitate. The solution was filtered and the solid rinsed with hexanes twice. The resulting solution was evaporated to half its original volume and stored at -35 °C for two days. The title compound crystallized out of solution as bright green crystals. The solution was filtered, the crystals isolated (661 mg) and the residue left to crystallize for an additional week at -35 °C yielding a second crop of pure crystals (258 mg) for a total of 919 mg (yield=48%). **^{1}H NMR** (500 MHz, benzene-*d₆*): δ 7.99 (s, broad, 1H, BH), 7.59 (d, $^3J_{H\text{-}H}$=8Hz, 2H, H3 or H6), 7.41 (d, $^3J_{H\text{-}H}$=8Hz, 2H, H3 or H6), 7.26 (t, $^3J_{H\text{-}H}$=8Hz, 2H, H4 or H5), 7.08 (t, $^3J_{H\text{-}H}$=8Hz, 2H, H4 or H5), 1.91-1.69 (m, 6H, 4H from H10 and 2H from H11), 1.57-1.47 (m, 6H, 4H from H10 and 2H from H11), 1.30 (s, 12H, H8 or H9), 0.91 (s, 12H, H8 or H9).**^{13}C{^{1}H}** (126 MHz, benzene-*d₆*): δ 154.4 (s, 2C, C2), 148.4 (s, broad, 2C, C1), 138.1 (s, 2C, C3 or C6), 131.6 (s, 2C, C3 or C6), 131.0 (s, 2C, C4 or C5), 124.8 (s, 2C, C4 or C5), 54.5 (s, 4C, C7), 42.0 (s, 4C, C10), 34.6 (s, 4C, C8 or C9), 25.6 (s, 4C, C8 or C9), 18.7 (s, 2C, C11).**^{11}B{^{1}H}** (160 MHz, benzene-*d₆*): δ 67.0 (s, 1B). Elemental analysis calcd. for $C_{30}H_{44}B_1N_2Cl_1$: C, 75.23; H, 9.26; N, 5.85%. Found: C, 75.01; H, 10.58; N, 5.92%.

bis(2-(TMP)phenyl)chloroborane•H_2 (2): 430 mg (0.9 mmol) of **1** were dissolved in *ca* 10 mL of hexanes in a sealed Schlenk vessel containing a Teflon coated stir bar. The atmosphere was removed from the vessel by three freeze pump thaw cycles and the vessel was pressurized with one atm of hydrogen. The reaction mixture was left to stir for 4 hours, resulting in a quasi-colorless solution with a white solid in suspension. The solid residue was isolated by filtration by two washes with hexanes

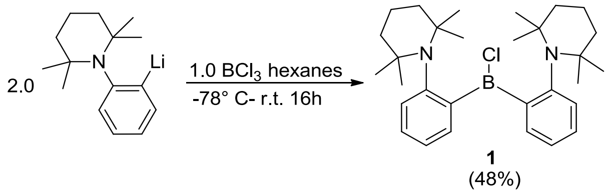
(5mL). 223 mg of solid was isolated. Yield=52%. **^{1}H NMR** (500 MHz, benzene-*d$_6$*): δ 10.47 (s, 1H, NH), aromatic protons: 8.25, 7.71, 7.63 (d, $^3J_{H-H}$=8Hz, 3H, H6, H18 and H21), 7.46, 7.37, 7.02, 6.88 (t, $^3J_{H-H}$=8Hz, 4H, H5, H6, H19 and H20), 6.79 (d, $^3J_{H-H}$=8Hz, 1H, H3); 5.04 (s, broad, 1H, BH); CH$_2$ aliphatic protons: 2.16-2.07, (m, 2H, 1H from H10, H12, H25 or H27 and 1H from H11 or H26), 1.86-1.73 (m, 3H, 2H from H10, H12, H25 or H27 and 1H from H11 or H26), 1.67-1.62 (m, 1H, H10, H12, H25 or H27), 1.47-1.22 (m, 5H, 4H from H10, H12, H25 or H27 and 1H from H11 or H26), 1.18-1.13 (m, 1H, H11 or H26); CH$_3$ aliphatic protons: 1.60, 1.58, 1.50, 1.12, 1.08, 0.98 (s, 24H, H8, H9, H14, H15, H23, H24, H29 and H30).**^{13}C{^{1}H}** (126 MHz, benzene-*d$_6$*): δ 151.1, 142.2 (s, 2C, C2 and C17); 138.6, 138.5, 131.3 (s, 3C, C6, C18 and C21); 127.4, 124.9, 124.8, 124.5 (s, 4C, C4, C5, C19 and C20); 120.9 (s, 1C, C3); 68.0, 67.5, 55.0, 54.5 (s, 4C, C7, C13, C22 and C28); 42.7, 42.3, 35.9, 35.3 (s, 4C, C10, C12, C25 and C27); 34.7, 33.8, 28.7, 28.1, 28.0, 27.9, 26.1, 26.0 (s, 8C, C8, C9, C14, C15, C23, 24, C29 and C30); 19.4, 15.8 (s, 2C, C11 and C26).**^{11}B{^{1}H}** (160 MHz, benzene-*d$_6$*): δ -1.9 (s, 1B). Elemental analysis calcd. for $C_{30}H_{46}B_1N_2Cl_1$: C, 74,92; H, 9.64; N, 5.82%. Found: C, 74,09; H, 9,70; N, 5.85%.

bis(2-(TMP)phenyl)borane (3): 300 mg (0.63 mmol) of **1** was dissolved in approximately 25 ml of THF and 50 mg (1.3 mmol, 2 equiv) of LiAlH$_4$ was added at room temperature resulting in complete loss of the characteristic bright green color of TMP$_2$BCl in few seconds. The mixture was left to stir for one hour after which time it was filtered and evaporated *in vacuo*. The resulting white solid was dissolved in approximately 25 ml of toluene and 1.4 mmol (2.2 equiv) of TMSBr was added. The mixture was left to stir overnight, resulting in a pale green solution. The mixture was evaporated and washed several times with hexane. After filtration and evaporation, 206mg, 74% yield of **3** was isolated as a pale sticky yellow solid. **^{1}H NMR** (500MHz, benzene-*d$_6$*): δ 7.40 (d, $^3J_{H-H}$=8Hz, 2H, H3 or H6); 7.37 (d, $^3J_{H-H}$=8Hz, 2H, H3 or H6); 7.16-7.11 (m, 2H, H4 or H5); 6.94 (t, $^3J_{H-H}$=8Hz, 2H, H4 or H5); 2.12 (s, broad, 2H, H10, H10’, H12 or H12’); 1.84 (m, 2H, H11 or H11’); 1.76 (s, broad, 2H, H10, H10’, H12 or H12’); 1.60-1.51 (m, 2H, H11 or H11’); 1.39 (s, broad, 10H: 6H from H8, H9, H14 or H15 and 4H from H10, H10’, H12 or H12’); 1.20 (s, broad, 12H, H8, H9, H14 and/or H15); 0.87 (s, broad, H8, H9, H14 or H15).**^{13}C{^{1}H}** (126 MHz, benzene-*d$_6$*): δ 153.2 (s, 2C, C2); 144.9 (s, broad, 2C, C1); 139.0 (s, 2C, C3 or C6); 132.2 (s, 2C, C3 or C6); 130.4 (s, 2C, C4 or C5); 123.9 (s, 2C, C4 or C5); 55.5 (s, broad, 2C, C7 or C13); 55.1 (s, broad, 2C, C7 or C13); 40.4 (s, broad, 4C C10 and C12); 35.5, 32.1, 27.5, 24.8 (s, broad, 8C, C8, C9, C14 and C15); 18.8 (s, 2C, C11).**^{11}B{^{1}H}** (160 MHz, benzene-*d$_6$*): δ 64.3 (s, 1B). No quality elemental analysis could be obtained for **3** and only data for the hydrolyzed compounds could be observed.

Preparation of **3** from **2**: In a J-Young NMR tube 15.0 mg of **2** (0.031 mmol) was dissolved in benzene and 1.05 eq of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (4.6 mg, 0.033 mmol) was added along with 3.0 mg of hexamethylbenzene as internal standard. 1 atm of H$_2$ was also added to limit the conversion back to **1** by H$_2$ release. The reaction was tracked by ^{1}H NMR, showing conversion **3** as the main product after 24h at room temperature (see SI for details).

Results and discussion

The addition of 2.0 equiv of [2-(2,2,6,6-tetramethylpiperidin-1-yl)phenyl]lithium[32] to a solution containing 1.0 equiv of BCl$_3$ in hexanes resulted in a drastic color change of the solution from colorless to very bright green. Crystallization from a hexane solution afforded bright green crystals of the novel compound **1** in 48% yield (Scheme 1). The compound displays a single broad (FWMH = 1000 Hz) ^{11}B{^{1}H} NMR resonance centered at δ = 64.3. Interestingly, the resonances associated to the methyl groups of the TMP moiety appear as four singlets in the ^{13}C NMR spectrum. This inequivalence can be attributed to the important steric congestion that results in an asymmetric conformation of the bridging aryl and TMP planes of symmetry (*vide infra*).



Scheme 1: Preparation of **1**.

The isolation of quality crystals of **1** allowed us to unambiguously determine the structure of the new FLP through an X-ray diffraction study. The ORTEP representation is presented in Figure 2. Indeed, it was found that, in contrast with **I** which dimerizes through bridging B-H,[44] the molecule is present as a monomer both in solid state and in solution. The molecule crystallized in the P_{CCN} space group adopting a slightly distorted geometry with two nitrogen centers facing each other. The identical distance between the Lewis basic nitrogen centers and the boron Lewis acidic center of 3.078 Å suggests that there is no significant bonding interaction between the active components of this FLP system. The sum of internal bond angles around the boron atom (360.1°) is indicative of a trigonal planar conformation. Moreover, the X-ray crystal structure shows that both TMP groups adopt the same conformation with the cycles in a chair conformation and two methyl groups pointing towards the boron moiety. Surprisingly, the aryl plane is not aligned with the symmetry plane of the TMP fragments The torsion angle between C1, C2, N1 and C11 of 17.4° is consistent with the inequivalence of the 4 methyl group in the ^{1}H and ^{13}C NMR.

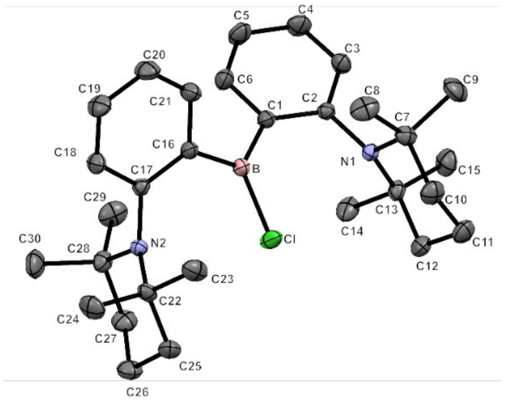
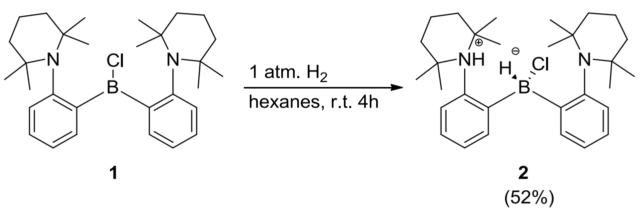


Figure 2: ORTEP drawing of **1** with anisotropic atomic displacement ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cl(1)-B = 1.7651(2); B-C(1) = 1.5719(1); C(2)-N(1) = 1.4323(1); C(1)-B-C(16) = 118.88(1); C(1)-B-Cl(1) = 120.56(7); C(2)-C(1)-B = 126.48(1); C(1)-C(2)-N(1) = 120.31(9).

The geometry of **1** was optimized by DFT at the ω-B97xD/6-31G** level of theory using the atomic coordinates of the crystal structure as input. The striking similarity between the crystal structure and the gas phase model supports the validity of the computational method (see SI for comparison). A Wiberg bond index (WBI) of 0.054 was calculated for the B-N bonds of **1**, further confirming the absence of significant bonding interactions between the Lewis acidic and basic moieties. Attempts to locate a minimum on the potential energy surface involving an intramolecular N-B bond systemically failed, resulting instead in the localization of two other conformers of **1**. Both isomers are thermodynamically accessible, being only 3.3 (1.8) and 6.2 (5.7) kcal.mol^{-1} higher in energy. Despite these conformers having a face-to-face orientation between the lone pair of nitrogen and the empty p_z orbital of boron, the WBIs of these conformers were found to be below 0.04, suggesting that no significant intramolecular bonding is present (see SI).

Dissolution of crystals of **1** in benzene-*d*$_6$ resulted in a bright green homogeneous solution. Exposure of the solution to 4 atm of hydrogen gas led to complete discoloration of the solution after 1 hour at room temperature. Analysis of the solution by NMR spectroscopy revealed an important shift of the signal in the $^{11}B\{^1H\}$ NMR spectrum from δ = 64.3 to δ = 1.94, a region characteristic of a tetrahedral environment at the boron center, along with a sharpening of the peak from a FWMH of 1000 Hz to 400 Hz. The broad resonances centered at δ = 5.03 and 10.14 in the ^1H NMR spectrum could be attributed to the hydride and proton fragments respectively, confirming the quantitative formation of a zwitterionic H_2 splitting product **2**.

Leaving the solution under an atmosphere of dinitrogen for 24 hours resulted in complete conversion back to **1.** Indeed, the splitting of hydrogen by **1** was calculated by DFT to be at -0.5 (-11.6) kcal.mol^{-1} from the reactants, with a transition state located at 19.2 (9.3) kcal.mol^{-1}. These values are in good agreement with rapid reversible H_2 splitting under ambient conditions. Even though **2** readily releases hydrogen, it was possible to isolate the zwitterion by exposing a hexanes solution of **1** to one atmosphere of H_2 for 4 hours. In these conditions, the green solution gradually discolored to become colorless, while a white solid precipitated. After filtration and washing of the residual solid with hexanes, **2** was isolated as a white powder in 52% yield (Scheme 2).



Scheme 2 : Preparation of compound **2** from **1**.

While the latter compound proved stable in the solid state, even under vacuum for several hours, its dissolution led to the release of dihydrogen, preventing us from obtaining quality crystals using traditional crystallization methods. However, by leaving a solution of **2** in a mixture of toluene/hexane for several days at -35 °C in a sealed vessel under four atm of H_2, quality crystals of **2** could be isolated, allowing us to unambiguously determine the structure of the new FLP through an X-ray diffraction study (Figure 2).

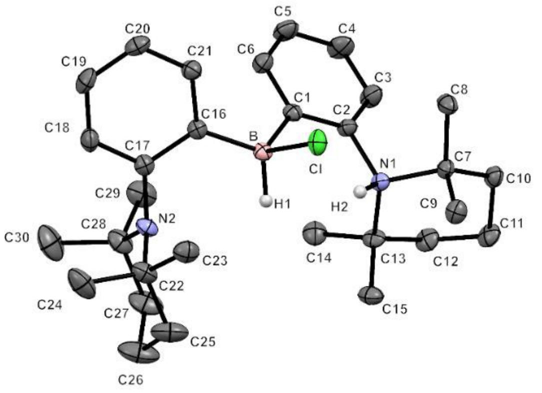
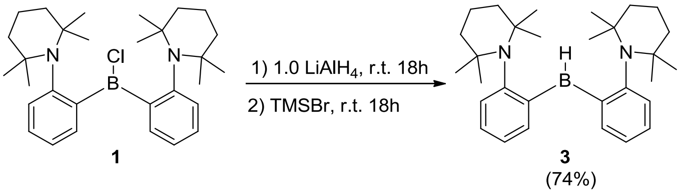


Figure 3: ORTEP drawing of **2** with anisotropic atomic displacement ellipsoids shown at the 50% probability level. Selected hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cl(1)-B(1) = 2.006(2); B(1)-C(1) = 1.635(2); B(1)-C(16) = 1.611(2); B(1)-H(1) = 1.11(2); C(2)-N(1) = 1.492(2); C(17)-N(2) = 1.440(2); C(1)-B(1)-C(16) = 115.5(1); C(1)-B(1)-Cl(1) = 105.6(1); C(2)-C(1)-B(1) = 123.6(1); C(17)-C(16)-B(1) = 125.2(1); C(1)-C(2)-N(1) = 117.8(1); C(16)-C(17)-N(2) = 119.9(1)

The sum of internal bond angles around the boron atom, while omitting the hydride, is of 327.9°, clearly indicating that the geometry around boron switch from trigonal planar in **1** to tetrahedral in **2**. Moreover, from **1** to **2**, the B-Cl bond elongated from 1.7651 Å to 2.006 Å and the B-C1 bond from 1.5719 Å to 1.611 Å. Unsurprisingly, the two TMP moieties exhibit notable differences. The C2-N1 bond is longer by 0.052 Å in comparison with the C17-N2 bond and by 0.060 Å with respect to the C2-N1 bond of **1**. The sum of internal angles around nitrogen (omitting the proton) is 344.1° for N1 compared to 352.0° for N2. Moreover, the TMP moieties adopt a different conformation with the protonated moiety being folded towards the aryl spacer. This type of conformational change has been previously observed with the related **C** FLP and is characteristic of a H_2 splitting adduct.[32] Interestingly, in the solid state, the proton is facing both the chlorine and hydride atoms, suggesting a possible electrostatic interaction between the proton and these two moieties. DFT studies revealed that an isomer in which the proton is directly facing the hydride (no apparent interaction with chlorine) is slightly endergonic (+2.0 (+2.5) kcal.mol^{-1})) with respect to the crystallized isomer.

The presence of the halogen at the boron center is of particular interest since the product of hydrogen splitting can then be regarded either as a simple hydrogen splitting product or as an HCl splitting product. Curious to see if it could be possible to remove the HCl fragment and generate the related hydroborane, **2** was dissolved in a benzene-*d*$_6$ solution containing 1.05 equivalent of the strong base 1,5,7-triazabicyclo[4.4.0]dec-5-ene. Following the reaction by ^1H NMR spectroscopy revealed transformation of **2** to **3** after 24 hours of reaction at room temperature (See SI).

In order to verify the nature of the product, **3** was synthesized independently from **1**. First, a solution of **1** was reduced with $LiAlH_4$ after which TMSBr was added, generating TMP_2BH in 74% yield (Scheme 3). Quality crystals of **3** were grown from a saturated toluene solution stored at -35 °C for several days.



Scheme 3: Independent preparation of **3** from **1**

In analogy to **1**, **3** also crystallizes in the P_{CCN} space group and the TMP groups adopt the same conformation (Figure 4). In fact, the structure is very similar to that of **1**, with the replacement of the chlorine atom for a hydrogen atom. However, the localization of the hydride could not be done precisely since it is disordered on two positions. However, in this case, most likely due to the reduced bulk of the hydrogen atom compared to chlorine, the aryl plane is almost perfectly aligned with the symmetry plane of the TMP fragments. The torsion angle between C1, C2, N1 and C11 is only 0.7° as compared to 17.4 ° for **1**, explaining that only two signals are observed by ^{1}H and ^{13}C NMR for the methyl groups on TMP. The structure of **2** was optimized in the gas phase using the geometric parameters of the crystal structure as input. Two similar energetically accessible conformers were also located on the potential energy surface but the Wiberg bond indexes being below 0.1 once again suggests that no significant bonding interaction is present between the boron and nitrogen centers (See SI).

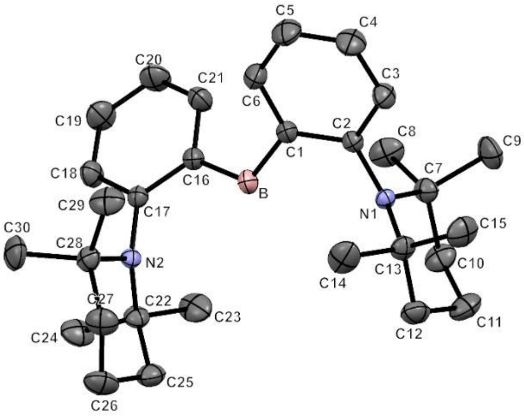


Figure 4: ORTEP drawing of **3** with anisotropic atomic displacement ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:C(2)-N(1) = B-C(1) = 1.5583(2); 1.4375(1); C(1)-B-C(16) = 120.83(2); C(2)-C(1)-B = 122.43(1); C(1)-C(2)-N(1) =118.46(9)

Unfortunately, **3** did not generate any new product upon reaction with hydrogen, even under four atm of H_2 pressure in benzene-*d₆*. The lack of an observable H_2 splitting product can be explained by the fact the product is thermodynamically uphill, having been calculated at 7.6 kcal.mol^{-1}. However, a transition state for dihydrogen splitting was found to be readily accessible at 15.9 (9.3) kcal.mol^{-1}. It is interesting to note that in the latter case the enthalpic aspect of the transition state is equivalent to the one observed for the reaction of **1** to **2**, but that the entropic component is significantly lower in presence of the hydride on boron rather than chloride, which is probably a consequence in the difference of steric bulk between the H and the Cl.

Contrasting with **I**, compound **1** failed to react with electron-rich heteroarenes such as N-methylpyrrole. Similarly, no apparent transformation took place in the presence of carbon dioxide, even in the presence of dihydrogen. The lack of reactivity could be explained by the steric protection offered by the two TMP moieties preventing the approach of substrates other than hydrogen, but such hypothesis remains hypothetical. Nonetheless, compounds **1**, **2** and **3** provide an interesting entry point into the chemistry of multidentate N-B based FLP systems and are currently the subject of further developments.

Conclusions

In summary, a novel multidentate N-B based FLP system was prepared and shown to readily activate dihydrogen in a quasi thermoneutral fashion. The compound and the hydrogen splitting product were both characterized by X-ray diffraction studies, despite the propensity of **2** to release H_2 in solution. Furthermore, HCl can be abstracted from **2** to generate **3**, which was also synthesized independently from **1** and characterized by X-ray diffraction. Current work is focused on generating a boronium based FLP by chloride abstraction in order to allow the simultaneous activation of multiple small molecules.

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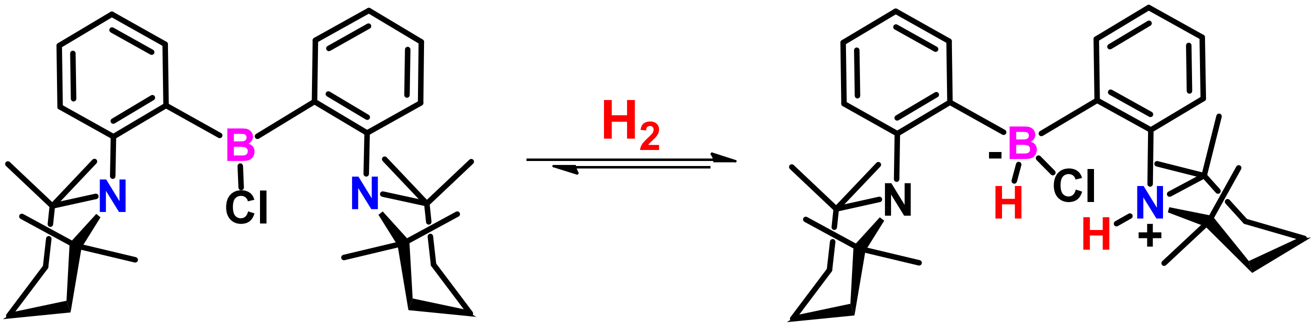
The FLP species bis(2-(TMP)phenyl)chloroborane (TMP=2,2,6,6-tetramethylpiperidine) (**1**) was prepared and crystallized as a monomeric Frustrated Lewis Pair (FLP) displaying no apparent B-N interaction. Species **1** readily reacts with H_2 at room temperature to generate reversibly the zwitterionic H_2 activation product **2**. Interestingly, in the presence of a base, **2** releases HCl, generating the novel FLP species **3** which is also monomeric.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