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# Replacing $C_6F_5$ groups with Cl and H atoms in frustrated Lewis pairs: $H_2$ additions and catalytic hydrogenations†

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2-(Dialkylamino)phenylboranes containing the BXZ group, where X, Z = $C_6F_5$, Cl, and H, were prepared in a few synthetic steps and demonstrated the cleavage of $H_2$ under mild conditions. Depending on the nature of the dialkylamino group, X, and Z, the stability of the produced zwitterionic $H_2$ adducts varies from isolated solids indefinitely stable in an inert atmosphere to those quickly equilibrating with the initial aminoborane and $H_2$. Using a combined experimental/computational approach on a series of isostructural aminoboranes (dialkylamino = 2,2,6,6-tetramethylpiperid-1-yl), it was demonstrated that the electronegativity and the steric effect of the substituents generally follow the trend $C_6F_5 \sim Cl \gg H$. This observation is useful for designing new FLPs for practical applications. As an example, we demonstrated the hydrogenation of alkynes to *cis*-alkenes under mild conditions that was catalyzed by a chloro-analogue of the $C_6F_5$-substituted aminoborane developed previously. The presence of a BHCl group in the aminochloroboranes or in their $H_2$ adducts features facile redistribution of the H and Cl atoms and the formation of polychloro and polyhydrido species.

## Introduction

High Lewis acidity and hydrolytic stability of (perfluoroaryl)boranes have uniquely positioned these compounds as catalysts in organic synthesis[1] and α-olefin polymerization.[2] Recently, such boranes in combination with sterically demanding amines and phosphines have shown unprecedented reactivities as components of frustrated Lewis pairs (FLPs).[3] Particularly, metal-free heterolytic $H_2$ splitting and its transfer to other organic molecules in a catalytic fashion have been fruitfully explored.[4]

Motivated by the development of cost-efficient and light weight FLPs for catalytic applications, we have been studying *ansa*-aminoboranes (where "*ansa*" refers to the close vicinity of amino and boryl groups), in which the $C_6F_5$ groups of the borane moiety are replaced with elemental substituents X (where X = H, halogens). Recently, we have reported two archetypical $C_6F_5$-substituted *ortho*-aminophenylboranes, **1a** and **2a** differing in the Lewis basic amino component (Fig. 1).[5] The presence of a highly sterically demanding 2,2,6,6-tetramethylpiperid-1-yl amino group (TMP) and a sterically accessible dimethylamino ($Me_2N$) group substantially affected the thermodynamics and the reactivity of $H_2$. Whereas **1a** produced an extremely thermally stable $H_2$ adduct, **2a** reacted with $H_2$ reversibly, showing smooth intramolecular protonation[6] and other unexpected behaviour. The replacement of a single $C_6F_5$ group with H in **2a** provided **2b** serving as a catalyst in an unprecedented metal-free selective hydrogenation of alkynes into *cis*-alkenes. Aminoborane **2b** has also been shown to insert readily into $sp^2$-C–H bonds of simple arenes and alkenes.[7] On the other hand, the complete replacement of the $C_6F_5$ groups in **1a** with hydrogens gave aminoborane **1b** that activates $H_2$ reversibly[8] and efficiently catalyses the C–H borylation of

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†Electronic supplementary information (ESI) available: Experimental procedures, NMR spectra, crystallographic data, and detailed computational analysis. Crystallographic data (excluding structure factors) for the structures reported in this work. CCDC 1511243 (**2c**), 912583 (**4c**), 912582 (**4e**), 912585 (**5c**), and 912584 (**5e**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt04649e

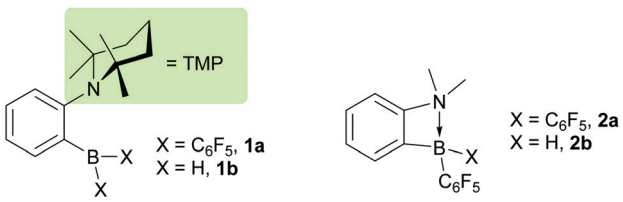



**Fig. 1** Previously reported 2-(dialkylamino)phenylborane FLPs.

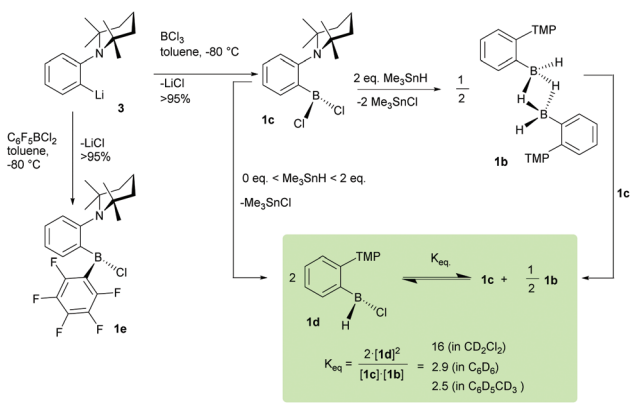
hetarenes with pinacolborane.[9] In continuation of our efforts, we report herein new *ansa*-aminoboranes, the derivatives of **1** and **2**, in which the $C_6F_5$ groups are partially or completely replaced with Cl or H atoms.[10] We studied $H_2$ addition to these aminoboranes following the established dichotomy between *ortho*-TMP- and *ortho*-$Me_2N$-phenylboranes such that the former defined general reactivity patterns, whereas the more labile and reactive $Me_2N$ compounds were used for catalytic implementations.

According to spectroscopic Lewis acidity scales, inorganic boranes $BX_3$ (X = H or halogen) have similar acidities to $B(C_6F_5)_3$.[11] These data are supported by experimental results on the $H_2$ splitting by FLPs comprising chloroboranes as the Lewis acidic component.[12] At the same time, comparative reactivity studies of isostructural FLPs with systematic $C_6F_5 \rightarrow Cl$ replacement at the Lewis acidic site and motivated by the development of catalytic applications have never been addressed previously and, therefore, are of particular interest.

## Results and discussion

### Synthesis and characterization of new *ansa*-aminoboranes

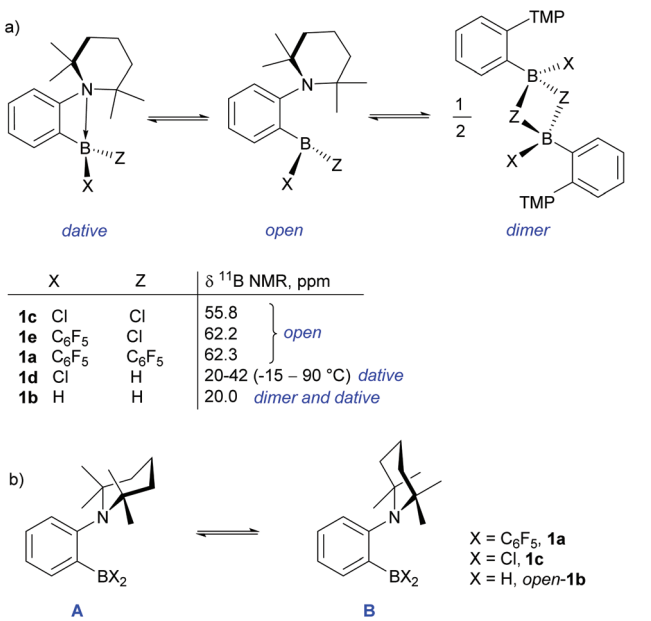
Chloroboranes **1c** and **1e** were prepared in one step starting from a readily available lithium compound **3**[5] and $BCl_3$ or $C_6F_5BCl_2$,[13] respectively (Scheme 1). Both aminoboranes were isolated in close to quantitative yields, similar to the previously reported **1a**. Apparently, high steric bulkiness of the TMP group suppressed the double addition of **3** to the starting boranes. Reduction of dichloroborane **1c** with 2 eq. of $Me_3SnH$[14] provides an alternative approach to a dimeric *ansa*-aminodihydroborane **1b** (Scheme 1) that was previously reported by us.[9] With smaller amounts of $Me_3SnH$, *ansa*-aminochloroborane **1d** is formed. In solution, it does not exist individually, but it forms an equilibrium with **1c** and **1b**. The equilibrium is instantly established at room temperature and even at −15 °C due to the rapid B–H/B–Cl exchange. The equilibrium state is slightly shifted to **1d** in aromatic hydrocarbons and strongly in more polar dichloromethane-$d_2$ and 1,2-dichloroethane (see the highlighted part of Scheme 1).[15]




**Scheme 1** Synthesis of aminoboranes **1b–1e**.

Frustrated aminoboranes can exist in several forms as illustrated in Scheme 2. The intramolecular N–B dative adducts and the μ-H-bridged dimeric species possess a reduced reactivity potential in comparison to the unquenched open structures. The aminoboranes **1a**, **1e**, and **1c** exist in their open forms as evident by the $^{11}B$ NMR shifts typical of non-coordinated boranes: 55.8, 62.2 and 62.3 ppm, respectively.[16] A combination of highly sterically demanding TMP and $B(C_6F_5)_2$ moieties in **1a** prevents the formation of an intramolecular N → B dative bond. Despite the smaller size of a chlorine atom as compared to the $C_6F_5$ group, both **1c** and **1e** have unquenched acid/base sites. In line with the experimental findings, DFT calculations predict *open* equilibrium structures for **1a**, **1e**, and **1c**.

The *closed* forms (*i.e.* four-membered ring structures with internal B–N dative bonds) could not be identified as energy minima on the potential energy surfaces. Computations point to the coexistence of two conformers for these aminoboranes with the phenylene bridge occupying either the equatorial (structure **A**) or the axial position (structure **B**, Scheme 2b) of the piperidine ring.[17] The former structure is predicted to be slightly more favoured for all aminoboranes **1a**, **1e**, and **1c** (for details, see the ESI†). Monochloroborane **1d** appears as a doublet in the $^{11}B$ NMR spectrum evidencing its monomeric form. Variable temperature (−12–90 °C, in toluene-$d_8$) $^{11}B$ NMR spectroscopy revealed a strong drift in the chemical shift of **1d** ($\delta$ = 20–42 ppm) attributed to a very rapid equilibrium between its open and dative forms, which is supported by calculations as well (see the ESI†). We showed previously that the *trans*-dimeric form of dihydroborane **1b** dominates in solutions whereas in the solid state it is the exclusive form as evident from X-ray diffraction analysis.[8]




**Scheme 2** (a) Appearance of *ansa*-TMP-phenylboranes as the *open* and the quenched forms; (b) conformational variation in compounds **1a–1c**.

### Addition of $H_2$ to the *ansa*-aminoboranes

As solutions in hydrocarbons or in chlorinated hydrocarbons, aminochloroboranes **1c**, **1e** and **1d** react with $H_2$ (2 bar) within the first few minutes at room temperature, producing the respective ammonium chloroborohydrides **4c**, **4e** and **4d**. Compounds **4c** and **4e** were isolated almost quantitatively as white crystalline powders indefinitely stable under an inert atmosphere.

Owing to the existing equilibrium between **1d**, **1c**, and **1b** in solutions, the reaction with $H_2$ "freezes" it to some extent, producing mixtures of chloroborodihydride **4d** contaminated with varying amounts of **4c** and **1b** (Scheme 3). Dichloromethane and 1,2-dichloroethane are advantageous solvents for producing mixtures rich in **4d** owing to the higher content of **1d** in these solvents. Previously, we reported that the addition of $H_2$ to *ortho*-TMP-dihydroborane **1b** is a rapid and thermodynamically nearly neutral process. The equilibrium can thus be shifted towards the $H_2$ adduct **4b** by using a more polar solvent, higher $H_2$ pressure and low temperatures (72% conversion in $CD_2Cl_2$, 10 bar $H_2$, −15 °C).[8]

The solid state structures of $H_2$ adducts **4c** and **4e** were determined using single crystal X-ray diffraction (Fig. 2). The structure of **4c** displays the proximity of the NH and BH hydrogens pointing to the existence of a dihydrogen bond similarly to that observed for analogous *ansa*-aminoborane-$H_2$ adducts.[5,18] Interestingly, the X-ray structure of **4e** does not involve this type of interaction, but instead, H···Cl bond formation is apparent. To characterize the structure of dihydrogen adducts **4a**, **4c–4e** in dichloromethane solution, the

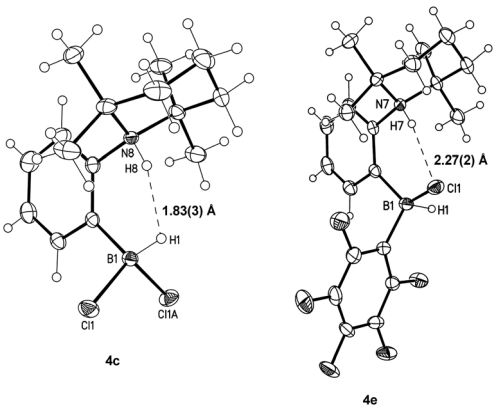



Fig. 2 Structures of chloroborohydrides **4c** and **4e** in a solid state (displacement parameters are drawn at the 50% probability level).

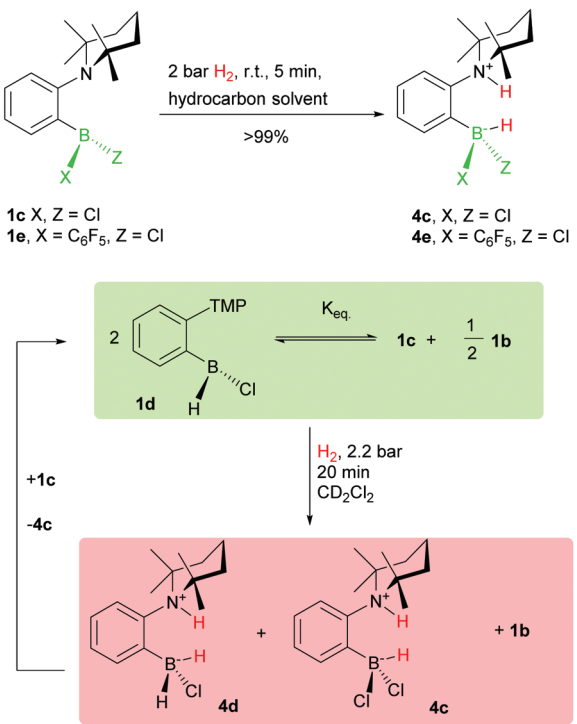
$H_N$–$H_B$ bond lengths were studied by 1D NOE $^1$H NMR spectroscopy and they were compared to data from DFT calculations (see the ESI† for details). Similarly to the solid state, a pronounced preference for the dihydrogen-bonded isomer in solution was established for **4c** by both methods. Adduct **4d** could not be isolated in the pure form, therefore, only solution-phase computational and NOE data are available, which indicate that dihydrogen-bonded species are clearly favoured in DCM solutions.

### Computational study of $H_2$ addition to *ansa*-aminoboranes 1a–c

The results reported above point to the similar reactivities of $C_6F_5$- and chloro-substituted *ansa*-aminoboranes, but also to a somewhat different behaviour of **1b**. To rationalize the observed reactivities, hydrogen addition to compounds **1a–1c** was studied by DFT calculations. The results are summarized in Fig. 3.

The structures of the transition states located along the $H_2$ splitting pathway (**$TS_{1a}$**, **$TS_{1b}$**, **$TS_{1c}$** in Fig. 3) share common features with those of the previously investigated FLP systems.[19] The slightly elongated H–H bond, the pyramidalization of the borane unit, and the typical end-on N···$H_2$ and side-on $H_2$···B arrangements of the reacting partners are all in line with the electron transfer reactivity model.[20] In the case of **1a** and **1c**, the activation barriers are fairly low ($\Delta G^{\ddagger}$ = 17.7 and 16.1 kcal mol$^{-1}$, respectively),[21] which is consistent with the observed reaction rates. Likewise, the thermodynamics of $H_2$ additions to **1a** and **1c**, resulting in **4a** and **4c**, are substantially exergonic and the computed reaction free energies are similar ($\Delta G_r$ = −12.0 and −11.1 kcal mol$^{-1}$). Although the open form of aminoborane **1b** is still rather reactive with an unprecedentedly low barrier (**$TS_{1b}$** is only 11.8 kcal mol$^{-1}$ above *open*-**1b** + $H_2$), the overall barrier is predicted to be slightly higher (20.5 kcal mol$^{-1}$) than those with **1a** and **1c**, which is clearly due to the reactant state stabilization arising from dimerization. For the same reason, the reaction with **1b** becomes thermodynamically less favoured as well (slightly endergonic in toluene).

Naturally, the trend obtained for the Gibbs free energies of the reaction is closely related to the variation of the Lewis




Scheme 3 Addition of $H_2$ to aminoboranes **1c**, **1d** and **1e**.

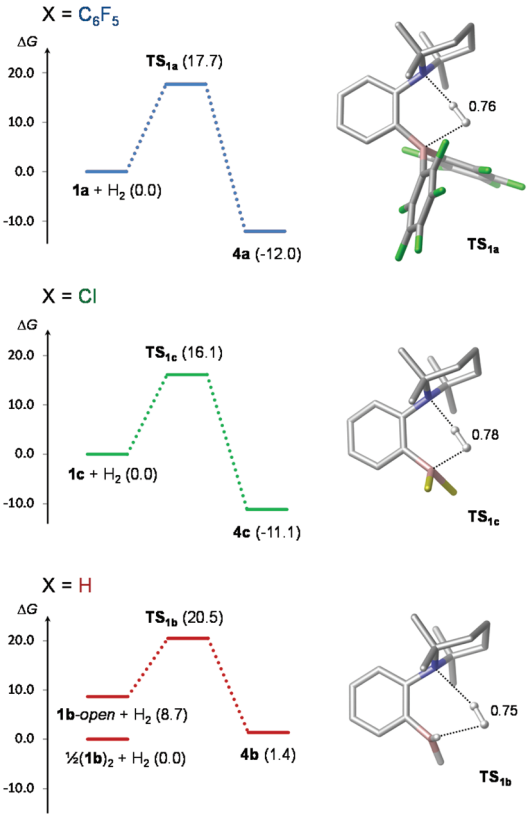
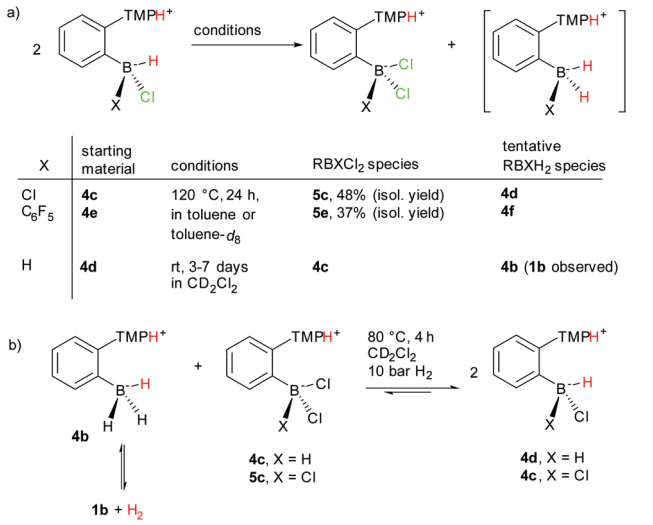



Fig. 3 Computed Gibbs free energy profiles for dihydrogen activation by **1a**, **1b** and **1c**. Relative stabilities are given in parenthesis (in kcal mol$^{-1}$; with respect to separated reactants; solvent = toluene). H–H bond distances are in Å (the bond length of free $H_2$ is 0.74 Å). In TS structures, CH hydrogens are omitted for clarity.




| X | starting material | conditions | $RBXCl_2$ species | tentative $RBXH_2$ species |
|---|---|---|---|---|
| Cl | **4c** | 120 °C, 24 h, in toluene or toluene-$d_8$ | **5c**, 48% (isol. yield) | **4d** |
| $C_6F_5$ | **4e** | | **5e**, 37% (isol. yield) | **4f** |
| H | **4d** | rt, 3-7 days in $CD_2Cl_2$ | **4c** | **4b** (**1b** observed) |

Scheme 4 (a) Decomposition of **4c**, **4e** and **4d** with the formation of chloroborates **5c**, **5e** and **4c**; (b) formation of **4c** and **4d** *via* "retrodismutation".

acidity of boryl units in the **1a–1c** series. In light of the hydride affinities of $B(C_6F_5)_3$, $BCl_3$ and $BH_3$ boranes ($\Delta G_{ha}$ = −72.5, −64.2 and −46.3 kcal mol$^{-1}$, respectively),[22] one expects somewhat larger differences between the thermodynamics of $H_2$ addition to the corresponding aminoboranes **1a**, **1c** and **1b**. However, our energy decomposition analysis reveals that the proton affinity of the TMP group is notably influenced by the nature of the boryl substituent, and also that the acid–base cooperativity taking place through the *ortho*-phenylene linker in these aminoboranes is an important factor.[23] This self-compensatory reactivity potential mechanism operating *via* a conjugated phenylene linker is a remarkable feature of the *ortho*-aminophenylborane FLPs.

### Thermal behaviour of $H_2$ adducts

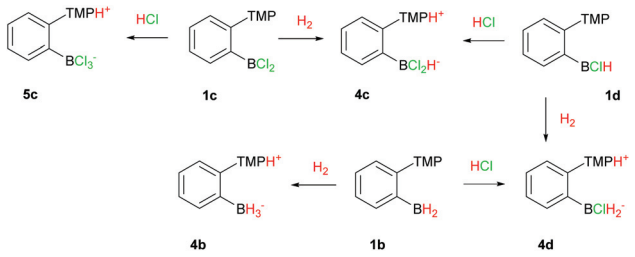
Unlike **4b**, $H_2$ adducts **4c–4e** do not demonstrate reverse hydrogen release, but instead they tend to decompose under certain conditions (Scheme 4). Compound **4d** has limited stability in $CD_2Cl_2$ solution dismutating to **4c** and presumably **4b** upon standing at room temperature for several days. Upon heating of **4c** or **4e** for 24 h at 120 °C in toluene, tri- **5c** and dichloroborate **5e** are isolated in 48% and 37% yields, respectively (Scheme 4a), as crystalline solids precipitating from the solution upon cooling (for X-ray structures, see the ESI†). The filtrate solution is a complex mixture of unidentified products, except for $C_6F_5H$, that is formed in an equimolar amount to **4e**, as evident from $^{19}F$ and $^{1}H$ NMR spectroscopies. We suggest that the B–H/B–Cl exchanging dismutation of **4c** and **4d** takes place at elevated temperatures and progresses until reaching the ultimate trichloro- **5c** and trihydroborate species **4b**, whereas **4b** decomposes into **1b** and $H_2$. Since **1b** is not detected among the products, we presume that it is unstable under harsh reaction conditions.

Additional evidence for such a decomposition pathway is provided by demonstration of a "retrodismutation" reaction: dichloroborohydride **4c**, aminoborane **1b** and $H_2$ produced **4d** upon heating for 4 h at 10 bar $H_2$ pressure and 80 °C. Similarly, the reaction between trichloroborate **5c**, **1b** and $H_2$ results in the formation of varying amounts of **4c** and **4d** with their ratio depending on the ratio of the starting materials. Trichloroborane **5c** can be completely converted into **4c** and **4b** provided **1b** is present in sufficient amounts (Scheme 4b).

The formation of the B–H/B–Cl exchange products during the addition of $H_2$ to the $ClB(C_6F_5)_2$/2,2,6,6-tetramethylpiperidine and $BCl_3$/2,6-dimethylpyridine FLPs was reported previously.[12] In the absence of the stabilizing factors, the easy redistribution of Cl and H atoms between chloro- and hydroborates seems to be a common reactivity pattern for these species. To gain deeper insight into the thermally-promoted transformations of 2-(TMP)-phenyl-chloroboranes and their adducts, we examined a series of reactions involving various $H_2$ and HCl addition/elimination steps computationally as shown in Scheme 5. The results are summarized in Fig. 4 in the form of a free energy profile.

It is apparent from this profile that the adduct **4c** lies in a free energy minimum with respect to $H_2$ and HCl elimination. The barrier towards $H_2$ elimination is notably lower, therefore




Scheme 5 Series of reactions investigated computationally.

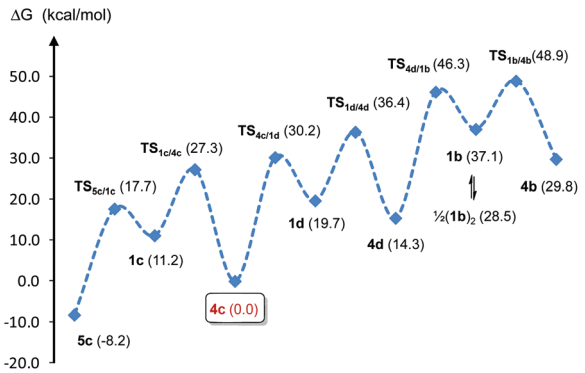



Fig. 4 Computed Gibbs free energy profile for the series of reactions shown in Scheme 5. The zero level of the diagram is arbitrarily chosen at **4c**.

**4c** → **1c** + $H_2$ might be the first step of the thermally induced transformation and decomposition. Although $H_2$ elimination from **4c** is unfavoured thermodynamically, this reaction may shift towards the formation of **1c** as $H_2$ is continuously discharged from the solution in these experiments.

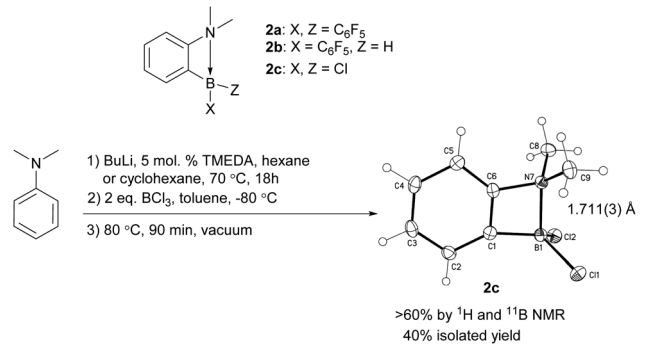
The reaction between **1c** and **4c** to produce **5c** and **4d** is thermodynamically feasible as calculations predict $\Delta G_r$ = 0.3 kcal mol$^{-1}$ in toluene and 1.4 kcal mol$^{-1}$ in DCM for this process. We found that this transformation can occur in a single step *via* a concerted $H^-/Cl^-$ exchange (for the identified transition states, see the ESI†). The related activation barrier is fairly high ($\Delta G^{\ddagger}$ = 30.2 kcal mol$^{-1}$ in toluene and 26.9 kcal mol$^{-1}$ in DCM), but it is consistent with the experimental conditions (120 °C, 24 h).

As for the destiny of the tentative **4f** formed *via* the H/Cl redistribution at the initial stage of **4e** thermolysis (Scheme 4a), we suggest that it decomposes by the intramolecular protonative splitting of the B–$C_6F_5$ bond that produces **1b** and $C_6F_5H$ as detected experimentally. Such a reaction was previously shown to proceed surprisingly easily in the *ortho*-aminophenylborane core.[6] Besides, we revised the thermal behaviour of compound **4a** and found that its decomposition *via* a similar protonative pathway becomes apparent at 150 °C (see the ESI† for details).

## Catalytic hydrogenations

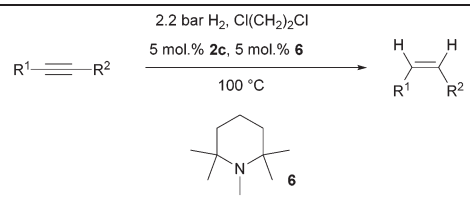
Recently, we have reported the highly *cis*-selective semihydrogenation of internal alkynes catalysed by *ansa*-aminohydroborane **2b** generated *in situ* from aminoborane **2a** (Scheme 6).[6] The *ansa*-phenylene junction of the active B and N centres in **2b** proved to be essential for such a catalytic activity based on the well-established reaction mechanism. Herein we report the similar catalytic activity of aminoborane **2c** (Table 1), a light weight chloro analogue of **2a**, prepared in 40% yield *via* a simple three-step protocol from inexpensive starting materials: *N*,*N*-dimethylaniline, butyllithium and boron trichloride (Scheme 6).

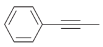
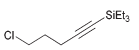
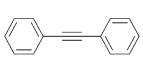
Internal alkynes were converted into respective *cis*-alkenes within 24 h or less at 100 °C and 2.2 bar $H_2$ using **2c** as a catalyst. Remarkably, sterically hindered amine 1,2,2,6,6-pentamethylpiperidine (**6**) serves as an efficient promoter enhancing




Scheme 6 *ansa*-Aminoboranes **2a** and **2b** reported recently to catalyse the hydrogenation of alkynes and the synthesis of the isostructural chloro-analogue **2c**. X-ray diffraction structure of **2c** (displacement parameters are drawn at the 50% probability level).

Table 1 *cis*-Selective semi-hydrogenation of internal alkynes catalysed by **2c**[a]




| Substrate | **2c**, mol% | Time, h | Conversion[b] (Isol. yield), % |
|---|---|---|---|
|  | 5 | 3 | 100 |
|  | 5 | 24 | 100 |
|  | 5 | 24 | 56 |
|  | 5 | 24 | 100 (90) |
|  | 10 | 24 | 92 |

[a] 125 ml Schlenk tube was charged with 0.5 mmol of alkyne, a catalytic amount of **2c** and **6** and 0.35 ml of 1,2-dichloroethane, pressurized with $H_2$ (2.2 bar) and stirred at respective temperatures. [b] Conversions were determined by the $^1$H NMR analysis of crude reaction mixtures.

the catalytic activity approximately two fold. Under standard conditions, only 5 mol% of both **2c** and **6** loadings are sufficient for reaching complete conversions of acetylenes. At the same time **2a** appears to be more catalytically active than **2c**, because the majority of substrates are completely hydrogenated with the aid of **2a** in 3 h at 80 °C. Regarding the feasibility of catalysis and high *cis*-stereoselectivity during hydrogenations, we suggest that the mechanism of catalysis by **2c** is very similar to the one previously reported for **2a**/**2b** though the details are yet to be established in the ongoing studies.

## Conclusions

In our present work, we studied structural analogues of previously reported frustrated 2-aminophenylboranes 2-($Alk_2N$)-$C_6H_4$-$B(C_6F_5)_2$, in which $C_6F_5$ groups were partially or completely replaced with H or Cl atoms. With the $Alk_2N$ group represented by 2,2,6,6-tetramethylpiperid-1-yl, all the considered aminoboranes react with $H_2$ within minutes at room temperature. We found strong similarities between $C_6F_5$-substituted and chloro-substituted boranes in their reactivities as well as the energetic and kinetic parameters of $H_2$ addition. At the same time, the replacement of $C_6F_5$ or Cl with H atoms leads to a significant drop in the reactivity potential, mainly due to the formation of the quenched forms of the starting B–H-substituted aminoboranes. This is consistent with the FLP concept as the compact size of the H atom cannot provide sufficient steric separation of the Lewis acidic and basic centres in the aminoboranes. On the other hand, our computations revealed a self-compensatory mechanism for this class of FLPs: more Lewis acidic boryl units diminish the basicity of the TMP group *via* the phenylene ring. Consequently, the energetics of $H_2$ addition to the aminoboranes that vary in the boryl part ($B(C_6F_5)_2$, $BCl_2$, $BH_2$) differs less than one expects from the comparison of the Lewis acidities of the corresponding parental boranes alone.

The attempted thermally promoted dehydrogenation of ammonium chloroborohydrides ($H_2$ adducts) leads to the redistribution of B–H and B–Cl substituents resulting in the isolation of polychloroborates **5c** and **5e**. These processes are feasible only under conditions when $H_2$ is discharged from the reaction as shown by the reversible formation of chloroborohydrides in "retrodismutation" experiments. For $C_6F_5$-substituted borates the decomposition involves protonative cleavage of the B–$C_6F_5$ bond yielding $C_6F_5H$. In the molecules of the studied ammonium chloroborohydrides, a protic hydrogen atom can be connected to either a Cl or H atom of the BH(Cl)X unit through intramolecular Cl···H or dihydrogen bonds. We found that these forms are usually nearly equal in energy and can be easily interconverted *via* rotation around the B–C bond.

Experimental and computational comparisons between isostructural chloro- and $C_6F_5$-substituted aminoboranes revealed a high degree of similarity in reactivities to $H_2$, which is reflected by the energetics of the overall reactions and transition states as well as by the stability of $H_2$ adducts. This similarity was pronouncedly demonstrated by the similar catalytic abilities of chloro- and $C_6F_5$-substituted aminoboranes **2c** and **2a** in the hydrogenation of alkynes. Simple and lightweight FLPs derived from boranes with elementary substituents are promising catalysts for hydrogenation and C–H borylation reactions and studies of their catalytic properties are currently in progress in our groups.

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