

PAPER

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2263Replacing C₆F₅ groups with Cl and H atoms in
frustrated Lewis pairs: H₂ additions and catalytic
hydrogenations†K. Chernichenko,^a B. Kótai,^b M. Nieger,^a S. Heikkinen,^a I. Pápai*^b and T. Repo*^a

2-(Dialkylamino)phenylboranes containing the BXZ group, where X, Z = C₆F₅, Cl, and H, were prepared in a few synthetic steps and demonstrated the cleavage of H₂ under mild conditions. Depending on the nature of the dialkylamino group, X, and Z, the stability of the produced zwitterionic H₂ adducts varies from isolated solids indefinitely stable in an inert atmosphere to those quickly equilibrating with the initial aminoborane and H₂. 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 electro-negativity and the steric effect of the substituents generally follow the trend C₆F₅ ~ Cl ≫ 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 C₆F₅-substituted aminoborane developed previously. The presence of a BHCl group in the amino-chloroboranes or in their H₂ adducts features facile redistribution of the H and Cl atoms and the formation of polychloro and polyhydrido species.

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Introduction

High Lewis acidity and hydrolytic stability of (perfluoroaryl)-boranes have uniquely positioned these compounds as catalysts in organic synthesis¹ 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 H₂ 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 C₆F₅ groups of the borane moiety are replaced with elemental substituents X

(where X = H, halogens). Recently, we have reported two archetypical C₆F₅-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 (Me₂N) group substantially affected the thermodynamics and the reactivity of H₂. Whereas **1a** produced an extremely thermally stable H₂ adduct, **2a** reacted with H₂ reversibly, showing smooth intramolecular protonation⁶ and other unexpected behaviour. The replacement of a single C₆F₅ 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 sp²-C–H bonds of simple arenes and alkenes.⁷ On the other hand, the complete replacement of the C₆F₅ groups in **1a** with hydrogens gave aminoborane **1b** that activates H₂ reversibly⁸ and efficiently catalyses the C–H borylation of

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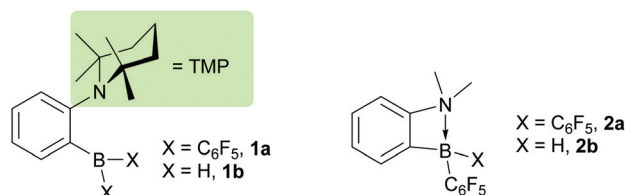
†Electronic supplementary information (ESI) available: Experimental procedures, NMR spectra, crystallographic data, and detailed computational analysis. Crystallographic data (excluding structure factors) for the structures reported in this work. CCDC 1511243 (**2c**), 912583 (**4c**), 912582 (**4e**), 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.

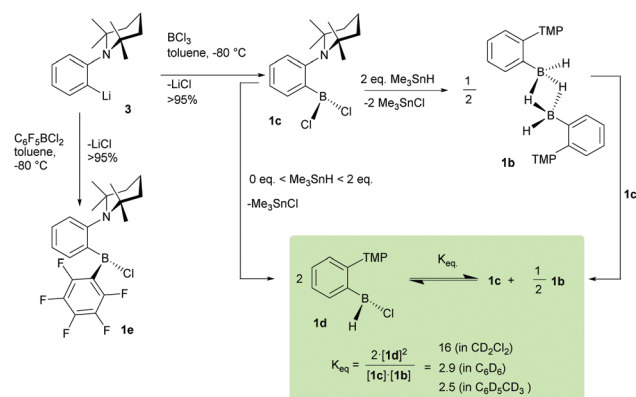
hetarenes with pinacolborane.⁹ In continuation of our efforts, we report herein new *ansa*-aminoboranes, the derivatives of **1** and **2**, in which the C₆F₅ groups are partially or completely replaced with Cl or H atoms.¹⁰ We studied H₂ addition to these aminoboranes following the established dichotomy between *ortho*-TMP- and *ortho*-Me₂N-phenylboranes such that the former defined general reactivity patterns, whereas the more labile and reactive Me₂N compounds were used for catalytic implementations.

According to spectroscopic Lewis acidity scales, inorganic boranes BX₃ (X = H or halogen) have similar acidities to B(C₆F₅)₃.¹¹ These data are supported by experimental results on the H₂ splitting by FLPs comprising chloroboranes as the Lewis acidic component.¹² At the same time, comparative reactivity studies of isostructural FLPs with systematic C₆F₅ → 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

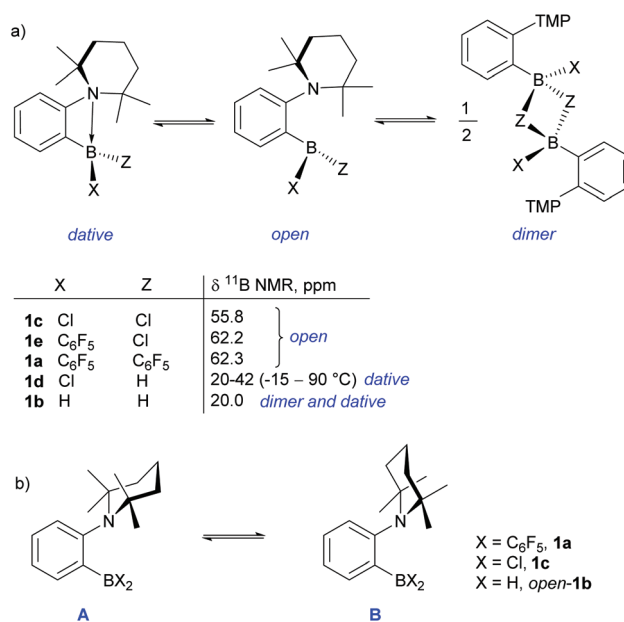
Chloroboranes **1c** and **1e** were prepared in one step starting from a readily available lithium compound **3**⁵ and BCl₃ or C₆F₅BCl₂,¹³ respectively (Scheme 1). Both aminoboranes were isolated in close to quantitative yields, similar to the previously reported **1a**. Apparently, high steric bulkiness of the TMP group suppressed the double addition of **3** to the starting boranes. Reduction of dichloroborane **1c** with 2 eq. of Me₃SnH¹⁴ provides an alternative approach to a dimeric *ansa*-aminodihydroborane **1b** (Scheme 1) that was previously reported by us.⁹ With smaller amounts of Me₃SnH, *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 ¹¹B 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(C₆F₅)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 C₆F₅ 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 ¹¹B NMR spectrum evidencing its monomeric form. Variable temperature (−12–90 °C, in toluene-*d*₈) ¹¹B NMR spectroscopy revealed a strong drift in the chemical shift of **1d** (δ = 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 H₂ to the *ansa*-aminoboranes

As solutions in hydrocarbons or in chlorinated hydrocarbons, aminochloroboranes **1c**, **1e** and **1d** react with H₂ (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 H₂ “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 H₂ to *ortho*-TMP-dihydroborane **1b** is a rapid and thermodynamically nearly neutral process. The equilibrium can thus be shifted towards the H₂ adduct **4b** by using a more polar solvent, higher H₂ pressure and low temperatures (72% conversion in CD₂Cl₂, 10 bar H₂, −15 °C).⁸

The solid state structures of H₂ 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-H₂ 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

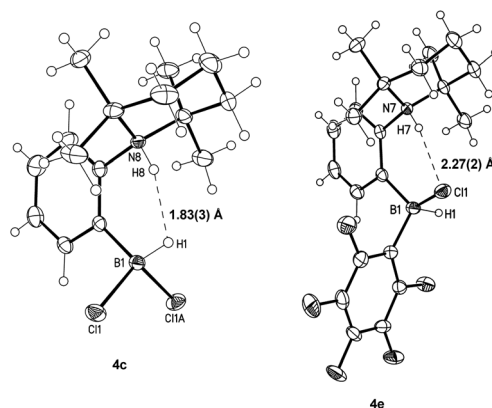


Fig. 2 Structures of chloroborohydrides **4c** and **4e** in a solid state (displacement parameters are drawn at the 50% probability level).

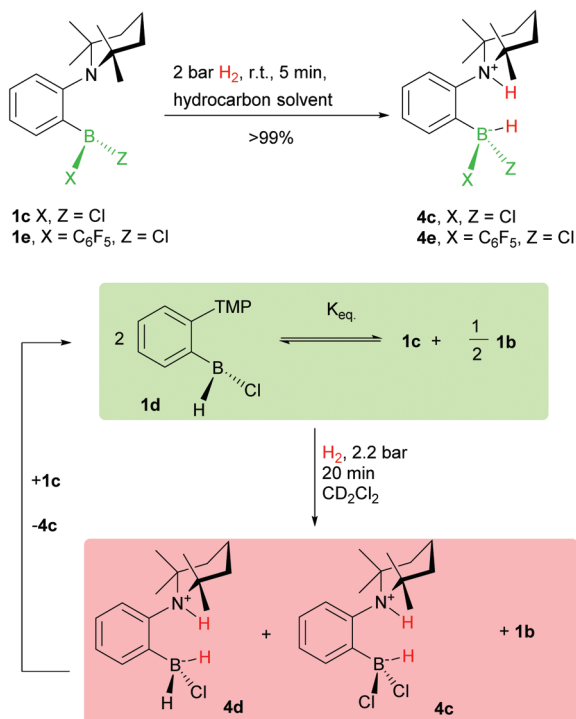
H_N–H_B bond lengths were studied by 1D NOE ¹H NMR spectroscopy and they were compared to data from DFT calculations (see the ESI† for details). Similarly to the solid state, a pronounced preference for the dihydrogen-bonded isomer in solution was established for **4c** by both methods. Adduct **4d** 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 H₂ addition to *ansa*-aminoboranes **1a–c**

The results reported above point to the similar reactivities of C₆F₅- 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 H₂ 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⋯H₂ and side-on H₂⋯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 H₂ 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* + H₂), 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 H₂ to aminoboranes **1c**, **1d** and **1e**.



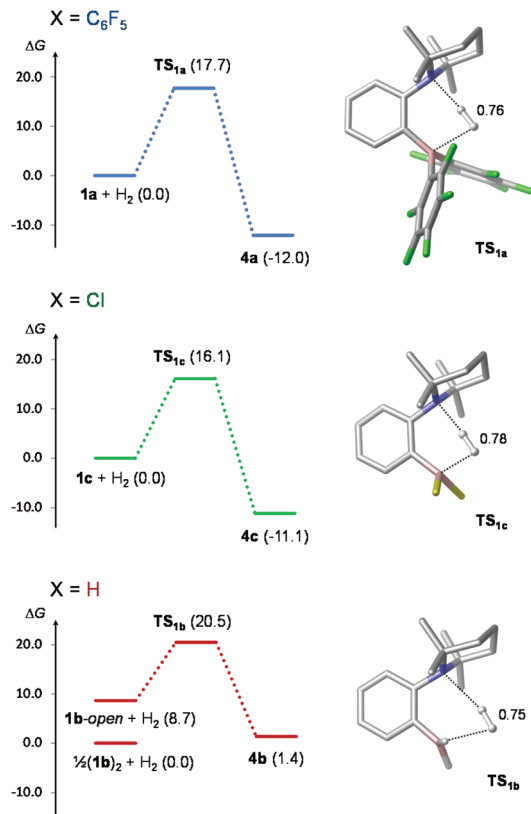
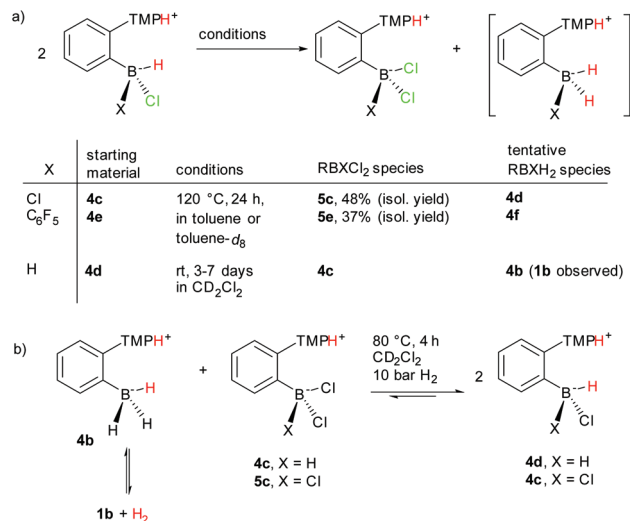


Fig. 3 Computed Gibbs free energy profiles for dihydrogen activation by **1a**, **1b** and **1c**. Relative stabilities are given in parenthesis (in kcal mol⁻¹; with respect to separated reactants; solvent = toluene). H-H bond distances are in Å (the bond length of free H₂ is 0.74 Å). In TS structures, CH hydrogens are omitted for clarity.

acidity of boryl units in the **1a–1c** series. In light of the hydride affinities of B(C₆F₅)₃, BCl₃ and BH₃ boranes ($\Delta G_{\text{ha}} = -72.5$, -64.2 and -46.3 kcal mol⁻¹, respectively),²² one expects somewhat larger differences between the thermodynamics of H₂ 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 H₂ adducts

Unlike **4b**, H₂ 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 CD₂Cl₂ 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



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".

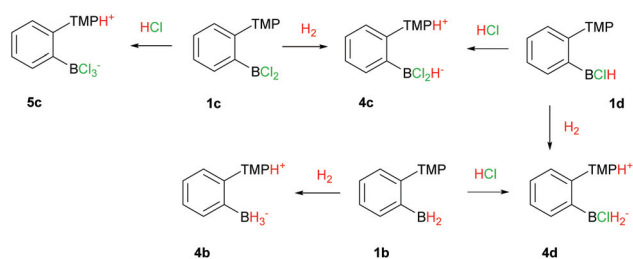
from the solution upon cooling (for X-ray structures, see the ESI†). The filtrate solution is a complex mixture of unidentified products, except for C₆F₅H, that is formed in an equimolar amount to **4e**, as evident from ¹⁹F and ¹H NMR spectroscopies. We suggest that the B-H/B-Cl exchanging dismutation 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 H₂. 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 H₂ produced **4d** upon heating for 4 h at 10 bar H₂ pressure and 80 °C. Similarly, the reaction between trichloroborate **5c**, **1b** and H₂ results in the formation of varying amounts of **4c** and **4d** with their ratio depending on the ratio of the starting materials. Trichloroborate **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 H₂ to the ClB(C₆F₅)₂/2,2,6,6-tetramethylpiperidine and BCl₃/2,6-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 H₂ 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 H₂ and HCl elimination. The barrier towards H₂ elimination is notably lower, therefore





Scheme 5 Series of reactions investigated computationally.

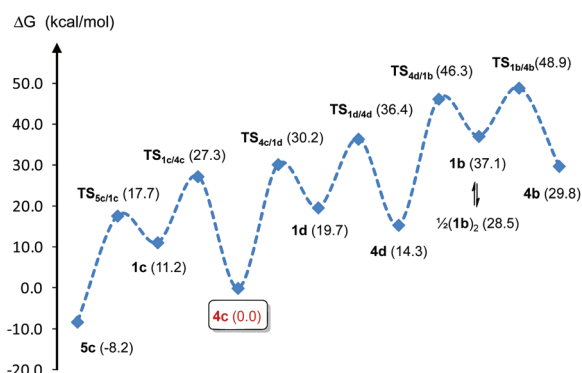


Fig. 4 Computed Gibbs free energy profile for the series of reactions shown in Scheme 5. The zero level of the diagram is arbitrarily chosen at **4c**.

4c → **1c** + H₂ might be the first step of the thermally induced transformation and decomposition. Although H₂ elimination from **4c** is unfavoured thermodynamically, this reaction may shift towards the formation of **1c** as H₂ 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 $\Delta G_r = 0.3 \text{ kcal mol}^{-1}$ in toluene and $1.4 \text{ kcal mol}^{-1}$ 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 ($\Delta G^\ddagger = 30.2 \text{ kcal mol}^{-1}$ in toluene and $26.9 \text{ kcal mol}^{-1}$ in DCM), but it is consistent with the experimental conditions (120 °C, 24 h).

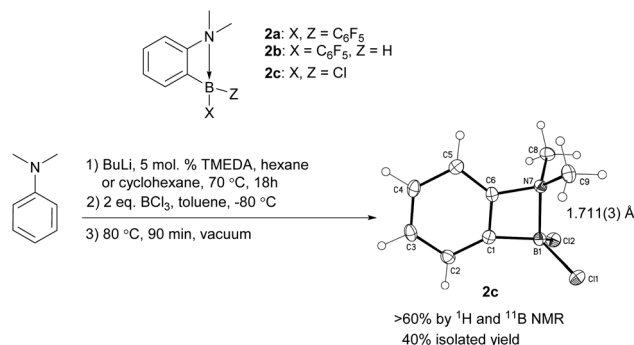
As for the destiny of the tentative **4f** formed *via* the H/Cl redistribution at the initial stage of **4e** thermolysis (Scheme 4a), we suggest that it decomposes by the intramolecular protonative splitting of the B–C₆F₅ bond that produces **1b** and C₆F₅H as detected experimentally. Such a reaction 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 H₂ 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

$\text{R}^1\text{—}\text{C}\equiv\text{C—R}^2 \xrightarrow[100\text{ }^\circ\text{C}]{2.2\text{ bar H}_2, \text{Cl(CH}_2)_2\text{Cl}, 5\text{ mol.}\% \text{ 2c}, 5\text{ mol.}\% \text{ 6}} \text{H—C=C—R}^1\text{—R}^2$			
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 H₂ (2.2 bar) and stirred at respective temperatures. ^b Conversions were determined by the ¹H 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-(Alk₂N)-C₆H₄-B(C₆F₅)₂, in which C₆F₅ groups were partially or completely replaced with H or Cl atoms. With the Alk₂N group represented by 2,2,6,6-tetramethylpiperid-1-yl, all the considered aminoboranes react with H₂ within minutes at room temperature. We found strong similarities between C₆F₅-substituted and chloro-substituted boranes in their reactivities as well as the energetic and kinetic parameters of H₂ addition. At the same time, the replacement of C₆F₅ 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 H₂ addition to the aminoboranes that vary in the boryl part (B(C₆F₅)₂, BCl₂, BH₂) 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 (H₂ 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 H₂ is discharged from the reaction as shown by the reversible formation of chloroborohydrides in “retrodismutation” experiments. For C₆F₅-substituted borates the decomposition involves protonative cleavage of the B-C₆F₅ bond yielding C₆F₅H. 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 C₆F₅-substituted aminoboranes revealed a high degree of similarity in reactivities to H₂, which is reflected by the energetics of the overall reactions and tran-

sition states as well as by the stability of H₂ adducts. This similarity was pronouncedly demonstrated by the similar catalytic abilities of chloro- and C₆F₅-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.

Acknowledgements

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