Replacing 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 a,b and T. Repo a, b

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 alkenes 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.

Introduction

High Lewis acidity and hydrolytic stability of (perfluoroaryl)boranes have uniquely positioned these compounds as catalysts in organic synthesis and α-olefin polymerization. Recently, such boranes in combination with sterically demanding amines and phosphines have shown unprecedented reactivities as components of frustrated Lewis pairs (FLPs). Particularly, metal-free heterolytic H₂ splitting and its transfer to other organic molecules in a catalytic fashion have been fruitfully explored.

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). 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 protonation 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 alkenes into cis-alkenes. Aminoborane 2b has also been shown to insert readily into sp²-C–H bonds of simple arenes and alklenes. On the other hand, the complete replacement of the C₆F₅ groups in 1a with hydrogens gave aminoborane 1b that activates H₂ reversibly and efficiently catalyses the C–H borylation of

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*Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014, Finland. E-mail: timo.repo@helsinki.fi
†Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2, H-1117 Budapest, Budapest, Hungary. E-mail: papai.imre@ttk.mta.hu
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Fig. 1 Previously reported 2-(dialkylamino)phenylborane FLPs.
hetarenes with pinacolborane. In continuation of our efforts, we report herein new ansa-aminoboranes, the derivatives of 1 and 2, where the C,F₅₂ groups are partially or completely replaced with Cl or H atoms. We studied H₂ addition to these aminoboranes following the established dichotomy between ortho-TMP- and ortho-Me₃N-phenylboranes such that the former defined general reactivity patterns, whereas the more labile and reactive Me₃N 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. These data are supported by experimental results on the H₂ splitting by FLPs comprising chloroboranes as the Lewis acidic component. 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 B(C₆F₅)₃ and BCl₃ or C₆F₅BCl₂, 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 Me₃SnH. Reduction of dichloroborane 1c with 2 eq. of Me₃SnH provides an alternative approach to a dimeric ansa-aminodihydroborane 1b (Scheme 1) that was previously reported by us. 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 substitution. The equilibrium state is slightly shifted to 1d in aromatic hydrocarbons and strongly in more polar dichloromethane-d₂ and 1,2-dichloroethane (see the highlighted part of Scheme 1).

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. 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. The former structure is predicted to be slightly more favoured for all aminoboranes 1a, 1e, and 1c (for details, see the ESIT). Monochloroborane 1d appears as a doublet in the ¹¹B NMR spectrum evidencing its monomeric form. Variable temperature (−12–90 °C, in toluene-d₈) 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 ESIT). 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.

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

**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).²

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 functionalities in the adduct (Fig. 2). 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 H₅–H₅ bond lengths were studied by 1D NOE ¹H NMR spectroscopy and they were compared to data from DFT calculations (see the ESIT 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 (TS₁a, TS₁b, TS₁c 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 (ΔG° = 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 (ΔG° = -12.0 and -11.1 kcal mol⁻¹). Although the open form of aminoborane 1b is still rather reactive with an unprecedently low barrier (TS₁b 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...
acidity of boryl units in the 1a–1c series. In light of the hydride affinities of B(C₆F₅)₃, BCl₃ and BH₃ boranes (ΔG_Ha = -72.5, -64.2 and -46.3 kcal mol⁻¹, respectively), 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. 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 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 4c, 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)₃/2,2,6,6-tetramethylpiperidine and BCl₃/2,6-dimethylpyridine FLPs was reported previously. 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
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 ΔG_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 (ΔG‡ = 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–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-aminoborane 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 trifluoride (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...
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)3, 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 sterics 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.

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Notes and references


Very recently, aminoborane Me₃N–C₆H₄–BH₂ was also synthesized by Fontaine et al., and it was shown to undergo a dehydrogenative B–B homocoupling reaction. See: (c) É. Rochette, N. Bouchard, J. L. Lavergne, C. F. Matta and F. G. Fontaine, Angew. Chem., Int. Ed., 2016, 55, 12722–12726.


14 We found Me₃SnH to be extremely efficient for the conversion of chloroboranes to hydroboranes. A by-product, Me₃SnCl, can be easily removed in a vacuum unlike when a more common tin hydride, Bu₂SnH, is used. For preparation of Me₃SnH, see: R. H. Fish, H. G. Kuivila and I. J. Tyminski, J. Am. Chem. Soc., 1967, 89, 5861–5868.


17 DFT calculations were carried out using the dispersion-corrected range-separated hybrid ωB97X-D functional along with the 6-311G(d,p) basis set as implemented in Gaussian 09. The electronic energies were refined by single-point energy calculations using a larger basis set (6-311+G (3df,3pd)). The SMD continuum model was employed to describe solvation. The reported energies refer to solvent-phase Gibbs free energies. For further details, see the ESL†.


21 Solution-phase Gibbs free energies reported in Fig. 2 and 3 refer to toluene as a solvent. Results obtained for DCM are provided in the ESL†.

22 The hydride affinity values were obtained from M05-2X calculations as described in our previous work. See: T. A. Rokob, A. Hamza and I. Pápai, J. Am. Chem. Soc., 2009, 131, 10701–10710.

23 For a detailed energy decomposition analysis, see the ESL†.