Theoretical studies of reactions with frustrated Lewis pairs

Final Report

1. The aim of the project

The recently emerging chemistry of sterically hindered Lewis acid/base pairs, the so-called frustrated Lewis pairs (FLPs) offers a new, transition metal free approach for the activation of small molecules, and this concept can be successfully applied in catalysis as well. The principal aim of the present project was to explore the mechanistic details of FLP mediated H-H or C-H bond activation processes, and utilize this knowledge in catalyst development. These transformations are of significant current interest in synthetic chemistry, because they provide alternative solutions to methods relying on the catalytic activity of precious transition metals. We used computational methods in our research, but the majority of our studies were carried out in collaboration with synthetic chemists, which has proven to be an efficient strategy in catalyst development. Herein, we present our contributions to these joint investigations.

During the course of this project we followed three major research lines as outlined in our original proposal, but meanwhile, additional FLP systems and conceptual issues became of interest, so our studies were extended accordingly. In our present report, we summarize the basic achievements of our project. The methodology of our computational approach has been described in the research program; all details are provided in the publications referenced for each research topic.

2. Results achieved in the project

2.1. Developing and testing simplified ansa-aminoboranes [1,2]

Ortho-phenylene bridged aminoboranes (i.e. *ansa*-aminoboranes) are known to have unique reactivity towards molecular hydrogen. In joint experimental-computational studies we have examined the reactivity of these intramolecular FLPs in collaboration with the Repo group (University of Helsinki).[1] In a follow-up study, the ability of *ansa*-aminoboranes to provide substantial NMR signal enhancement via parahydrogen-induced polarization was demonstrated (PHIP) [1]. The aminoborane possesing the BH_2 boryl unit was reacted with parahydrogen-enriched H_2 and the samples were subject to NMR measurements. Spin saturation transfer (SST) experiments allowed us to determine the reaction kinetic parameters and the relaxation times for a series of *ansa*-aminoboranes. Computations revealed that the measured and unusually large J_{HH} coupling constants are due to the presence of dihydrogen bonds formed between the oppositely charged NH and BH hydrogens in the adduct species (see Figure 1).

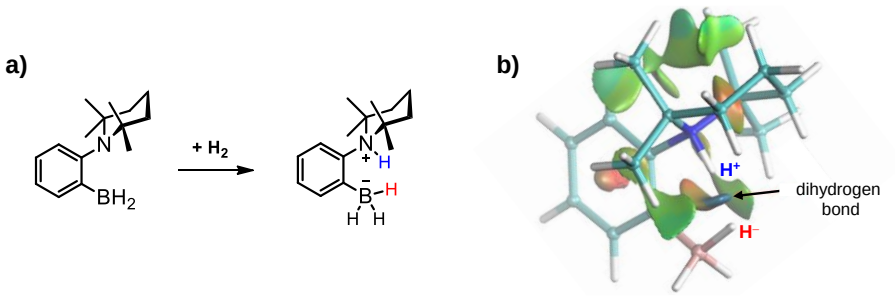


Figure 1: *H_2 activation with an ansa-aminoborane (a); NCI plot illustrating the dihydrogen bond in the adduct species (b).*

[1] For previous joint studies, see: a) K. Chernichenko, A. Madarász, I. Pápai, M. Nieger, M. Leskelä, T. Repo, *Nat. Chem.* **2013**, *5*, 718; b) K. Chernichenko, B. Kótai, I. Pápai, V. Zhivonitko, M. Nieger, M. Leskelä, T. Repo, *Angew. Chem. Int. Ed.* **2015**, 54, 1749-1753.

Structural analogues of previously reported *ansa*-aminoboranes (R_2N)-C_6H_4-$B(C_6F_5)_2$, in which the C_6F_5 groups were partially or completely replaced with H or Cl atoms were prepared and their reactions with H_2 were examined both experimentally and computationally (Figure 2) [2]. We found strong similarities between C_6F_5-substituted and chloro-substituted boranes in their reactivities, as well as in the thermodynamic and kinetic parameters of H_2 addition. However, the replacement of C_6F_5 or Cl with H atoms leads to a significant drop in the reactivity. This can be rationalized by the formation of the quenched forms of the starting B–H-substituted aminoboranes, which is consistent with the FLP concept: 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.

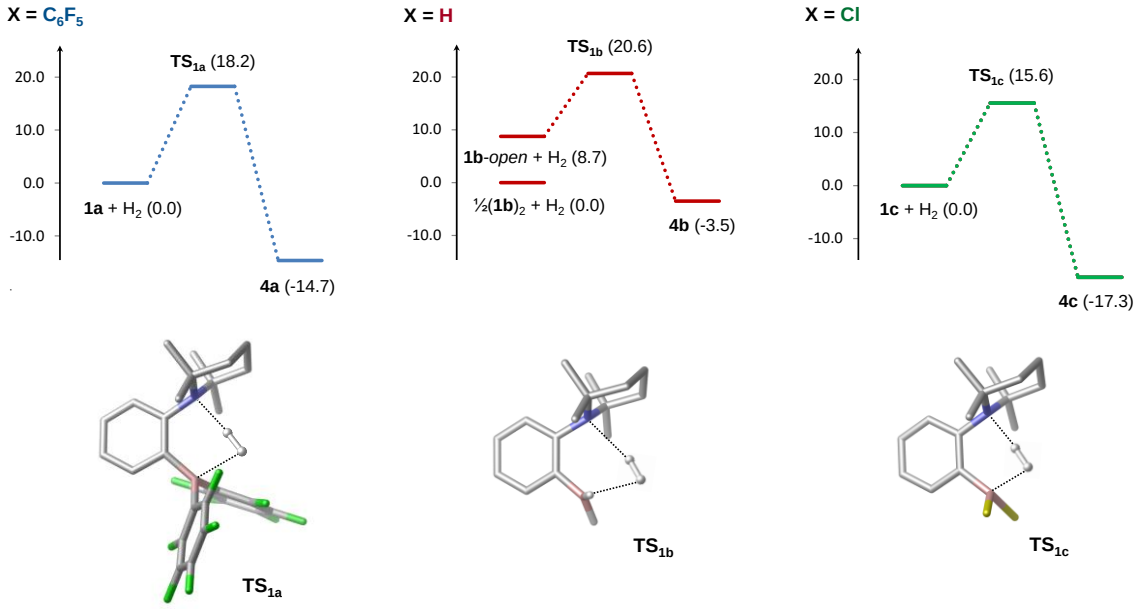


Figure 2: *Computed Gibbs free energy profiles for dihydrogen activation by ansa-aminoboranes* TMP-C_6H_4-BX_2, *X = C_6F_5 (**1a**), H (**1b**) and Cl (**1c**). Relative stabilities are given in kcal/mol. CH hydrogens are omitted for clarity.*

We found similarities in the catalytic behaviour of chloro- and C_6F_5–substituted aminoboranes as well, which could be demonstrated in the hydrogenation of alkynes.

2.2. C-H bond activation with FLPs [3-5]

We demonstrated that *ortho*-phenylene linked aminoboranes induce C-H activation in a variety of arenes and alkenes including the relatively unreactive benzene and hex-1-en [3]. Computations confirm that the metal-free C-H insertion proceeds via a frustrated Lewis pair mechanism involving heterolytic splitting of the C-H bond by cooperative action of the amine and boryl groups, which is followed by H_2 elimination (see **TS**$_{CH}$ and **TS**$_{elim}$ in Figure 3).

Of these two steps, the C-H activation is found to have a higher barrier and the predicted height is consistent with the elevated temperature required for this reaction. The overall borylation reaction is predicted to be endergonic implying that the reaction is unfavored in a closed system, however, the continuous release of the gaseous H_2 from the solution phase shifts the equilibrium towards the borylation product. We suggest that the primary factor that enables such reactivity is the optimal geometrical arrangement of the N and B centers connected by the rigid phenyl bridge in the *ansa* system. This common reactivity pattern serves as a platform for various catalytic reactions such as C-H borylation and hydrogenation of alkynes.

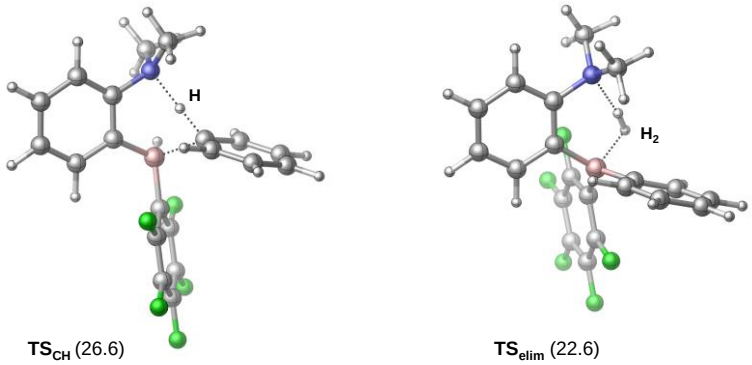
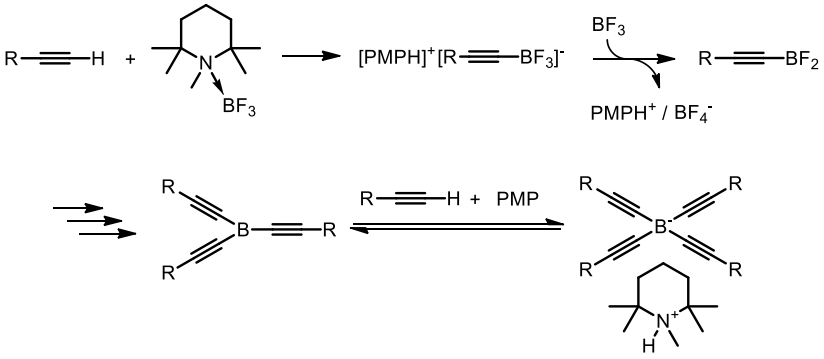


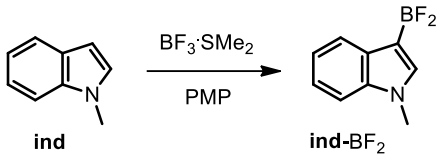
Figure 3: *C-H activation and H_2 elimination transition states identified computationally for the reaction of aminoborane Me_2N-C_6H_4-BH(C_6F_5) with benzene. Relative stabilities are given in kcal/mol with respect to the reactants.*

In a subsequent work, the sterically demanding amine, pentamethylpiperidine (PMP), was shown to form an isolable, but highly reactive Lewis acid–base adduct with borane BF_3 [4]. Computational analysis was carried out to screen various tertiary amines in terms of their electronic and steric properties, both important to achieve sufficient FLP-type reactivity. The PMP/BF_3 pair reacts with terminal acetylenes to give the products of C(sp)-H borylation, previously unknown tri- and tetraalkynylboron compounds (Scheme 1). Trialkynylfluoroborates can serve as surrogates of alkynyltrifluoroborates for C-C coupling reactions. Combining the discovered borylation reactivity with the PMP recovery provides a straightforward and atom-efficient approach to synthetically useful alkynylfluoroborates.



Scheme 1: *C–H borylation of terminal acetylenes with PMP/BF_3.*

The developed methodology was later extended to the borylation of more challenging C(sp^2)–H bonds. Namely, the borylation of electron rich N-heterocycles such as indoles, pyrroles and importantly indolenines by the BF_3·SMe_2 pair could be demonstrated experimentally (Scheme 2) [5]. These reactions require sterically hindered amines (such as PMP) and they are promoted by catalytic amounts of various thioureas.



Scheme 2: *C–H borylation of N-methylindole with PMP/BF_3·SMe_2.*

The mechanism of this reaction was examined computationally. Various activation pathways for the borylation of N-methylindole were considered, of which the FLP-type C-H activation mechanism was found to be the most feasible (see Figure 4). Along this mechanistic pathway, the

addition of BF_3 and the deprotonation of the substrate takes place concertedly (**TS**$_{FLP}$). This step is then followed by a fluorine shift from the adduct intermediate to an additional BF_3 molecule (**TS**$_{Ftrans}$) to form the BF_4^-/$PMPH^+$ salt. The borenium mediated mechanism represents an alternative pathway, but this could be ruled out due to very high computed barrier.

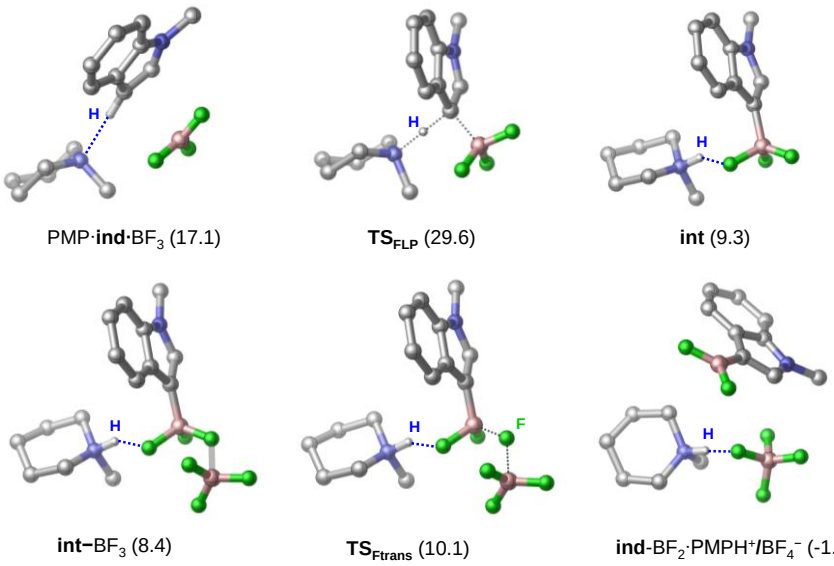


Figure 4: *FLP-type mechanism of C–H borylation of N-methylindole with PMP/BF_3·SMe_2.*

Computations provided insight into the role of thioureas as well. The results suggest that the presence of thiourea opens an alternative reaction pathway involving a borenium intermediate, which becomes competitive to the FLP-type mechanism, in particular at higher conversion rates, when most of the PMP is consumed.

2.3. Tuning the Lewis acidity of boranes [6-8]

The high reactivity of FLPs is very often incompatible with common functionalities of the substrate molecule, therefore successful catalytic applications require proper tuning of Lewis acid/base properties of components. Fine-tuning the electronic and steric properties of boranes is synthetically challenging, but it has proven to be a fruitful strategy that improved the functional group tolerance and lead to water tolerant FLP hydrogenation methods.[2] In continuation of our internal collaboration with the Soós group, we examined the effect of various substitutions in triaryl-boranes on their acidic properties.

A series of halogenated triaryl-boranes with a general BX_2Y formula was prepared and comprehensively characterized using combined experimental and theoretical methods [6]. This series of boranes has a default sterical setting around the boron center and their electronic properties are systematically varied by using F and/or Cl substituents in the *meta* and *para* positions of the X and Y aryl rings (Figure 5). We have shown that the calculated hydride affinity is a useful tool to quantify the electronic effects on Lewis acidity and predict the hydrogenation capacities of these boranes. As a general trend, the H/F replacement in meta-positions resulted in a significant enhancement of Lewis acidities, however, the H/Cl replacements on the bulkier aromatic ring have only negligible effects. These observations reveal important properties that affect the Lewis acidity and FLP reactivity and can guide future catalyst developments.

[2] For previous contributions, see: a) G. Erős, H. Mehdi, I. Pápai, T. A. Rokob, P. Király, G. Tárkányi, T. Soós, *Angew. Chem. Int. Ed.* **2010**, *49*, 6559; b) G. Erős, K. Nagy, H. Mehdi, I. Pápai, P. Nagy, P. Király, G. Tárkányi, T. Soós, *Chem. Eur. J.* **2012**, *18*, 574; c) Á. Gyömöre, M. Bakos, T. Földes, I. Pápai, A. Domján, T. Soós, *ACS Catal.* **2015**, *5*, 5366.

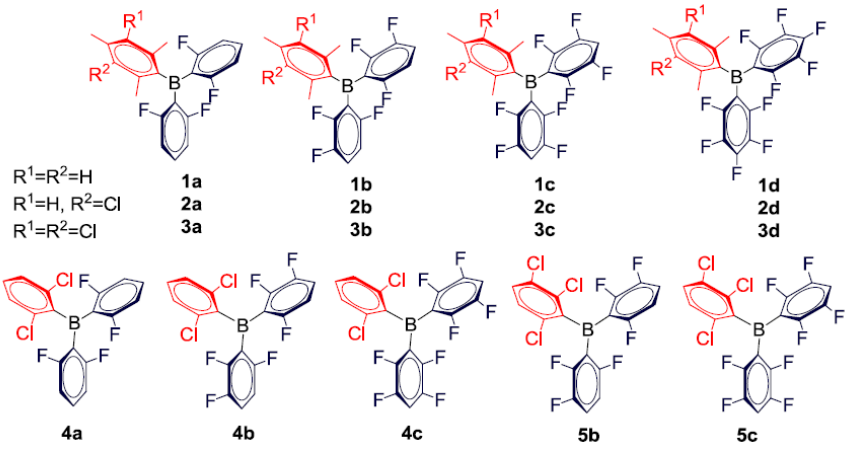


Figure 5: *Halogenated BX_2Y triaryl-boranes investigated experimentally and computationally.*

Systematic steric tuning of halogenated boranes revealed that the modulation of back-strain is an important design element to tackle water inhibition, which represents one of the key constrains in FLP-type hydrogenation reactions. DFT calculations on a series of boranes having different number of F and Cl substituents on the borane aromatic ring demonstrated that the hydride affinity is determined by the electronic effect and the steric penalty emerging upon the pyramidalization of the boron, i.e. the back-strain. The enhanced back-strain of the borane upon complexation makes water binding increasingly reversible, which maintains the preferential hydrogen activation ability while suppressing the interference of the water with FLP. The utility of this structurally fine-tuned borane was demonstrated in reductive amination of carbonyls [7].

The structure and dynamic behavior of classical Lewis pair adducts formed in the mixtures of piperidine (**pip**) and asymmetrically halogenated boranes (Figure 6) were examined using ^{19}F NMR spectroscopy and DFT calculations [8]. Computations revealed multiple conformational states of the adducts that differ in the orientation of the aryl groups and in the position of the halogen substituents.

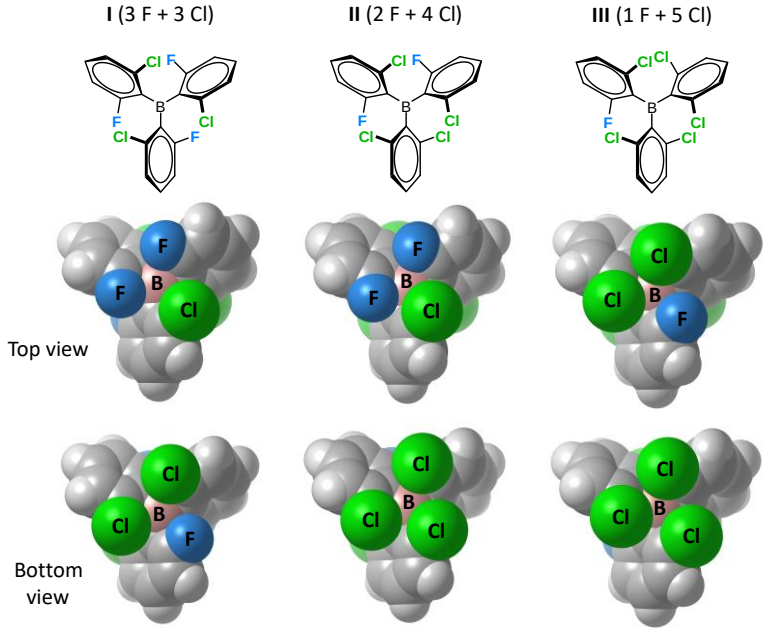


Figure 6: *Asymmetrically halogenated triaryl-boranes investigated experimentally and computationally in terms of their Lewis acidity.*

Based on the computed Gibbs free energy data, the affinity of the boranes for dative bonding with **pip** follows the order of **III** < **II** < **I,** which demonstrates the importance of back-strain in adduct formation. For each **pip**-borane complex, the energetically lowest lying conformational states are predicted to have similar stabilities implying that these forms could be all present simultaneously in solution, and they are expected to by in a dynamic equilibrium. These predictions could be verified by NMR investigations, namely via $^{19}F–^{1}H$ HOESY and ^{19}F EXSY experiments. Our results suggest that the conventional notion of Lewis acidity can be extended by assigning multiple acidity strengths to asymmetrically halogenated triaryl boranes.

2.4. Comparison of static and dynamic FLP reactivity models [9]

The remarkable reactivity of FLPs is generally associated with cooperative interactions between the unquenched Lewis pair and the reactant molecule. The mechanism of H_2 activation has been of particular interest, and our earlier computational studies provided valuable insight into the FLP concept and allowed us to formulate a simple reactivity model, which is referred to as the "electron transfer" model.[3] However, recent reports using *ab initio* molecular dynamics (AIMD) simulations suggested that the H_2-splitting process in the FLP-mediated hydrogen activation could be more eventfull than thought previously. In light of these new developments, we decided to reinvestigate some of the previously studied FLP + H_2 reactions with AIMD simulations. We explored the free energy surfaces of the hydrogen activation in terms of the two selected collective variables using metadynamics as a sampling technique (Figure 7) [9].

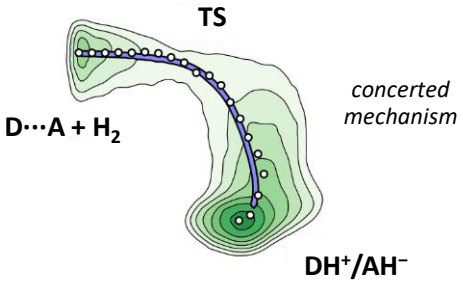


Figure 7: *Free energy surface obtained from AIMD metadynamics simulations carried out for H_2 activation with an unquenched Lewis donor/acceptor (D/A) pair.*

Our results confirm that the cleavage of H_2 by intramolecular FLPs takes place in a single concerted step, in agreement with earlier static quantum chemical calculations. In contrast to previous AIMD studies, no intermediate states could be located on the reaction free energy surfaces in our present work. These results demonstrates that the previously proposed simple mechanistic picture of FLP-mediated H_2 cleavage remains plausible in a finite temperature dynamic model as well. Statistical analysis carried out for a large number of reaction trajectories reveals notable asynchronicity in the development of donor-H and acceptor-H bonds with the latter being in a more advanced phase. As a consequence of asynchronicity, the excess kinetic energy released upon H_2 cleavage is stored in the form of donor-H bond vibrations, which may influence the outcome of catalytic hydrogenation.

2.5. Asymmetric hydrogenation of unsaturated compounds [10-11]

Utilization of chiral FLP catalysts in direct asymmetric hydrogenation of unsaturated compounds is a potential metal-free strategy in stereoselective synthesis. Remarkable developments have been achieved along this line over the past decade, however, the current level of comprehension concerning the stereoselectivity governing factors in these catalytic processes is not sufficient thus far to

[3] For reactivity models of hydrogen activation with FLPs, see: T. A. Rokob, I. Bakó, A. Stirling, A. Hamza, I. Pápai, *J. Am. Chem. Soc.* **2013**, *135*, 4425.

facilitate new catalyst design. The origin of stereoinduction in direct hydrogenation of imines catalyzed by a set of chiral, pinene and camphor derived boranes was examined computationally (Figure 8) [10].

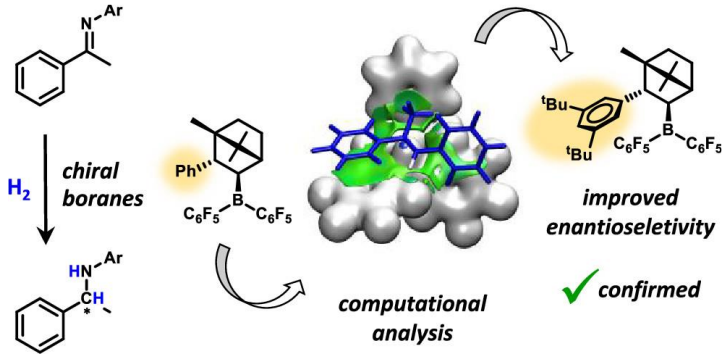


Figure 8: *Computational analysis of the origin of enantioselectivity in borane catalyzed hydrogenation of imines.*

The enantioselectivities predicted by the applied computational approach are in very good agreement with previous experimental observations reported by the Klankermayer group. Our analysis suggests that the stereoselectivity is governed by a thermodynamically less favored conformer of the borohydride intermediate, and not by the experimentally observed form. The most favored hydride transfer transition states are stabilized by specific aryl-aryl and alkyl-aryl noncovalent interactions, which play an important role in stereoinduction. The new computational insight was exploited in proposing new borane variants to improve the enantioselectivity, which could be demonstrated experimentally. One of the synthesized new boranes was shown to be a robust and efficient FLP catalyst in imine hydrogenation providing *ee*s above 90%, which could only be achieved so far at significantly lower temperature.

The new insight regarding the nature of the reactive borohydride intermediate inspired us to re-examine the stereoselectivity determining hydride transfer step in the asymmetric hydrogenation of enamines catalyzed by a chiral binaphthyl-linked aminoborane. These reactions were found to take place readily at mild conditions with a wide variety of structurally different substrates providing enantioselectivities up to 99% ee.[4] Indeed, we found a new and kinetically more favored reaction pathway for the hydride transfer step, which could account more satisfactorily for the remarkable enantioselectivity observed experimentally. Calculations were also carried out for the reaction with a more challenging (smaller) enamine substrate and the results are consistent with the measured *ee*s as well. Aromatic π-π stacking interactions between the catalyst's C_6F_5 substituent and the phenyl group of the enamine substrate were found to be crucial in stereoinduction (see Figure 9) [11].

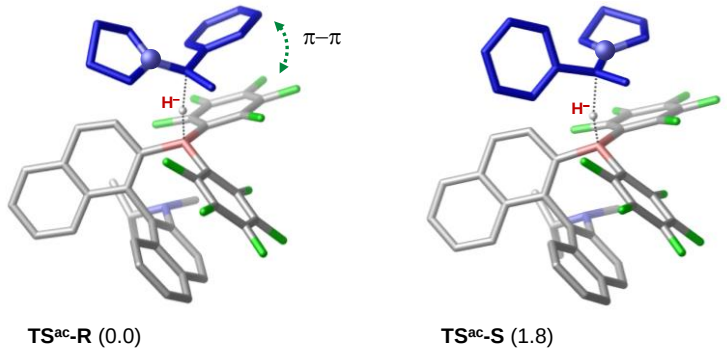


Figure 9: *Diastereomeric TSs in asymmetric hydrogenation of enamines (relative stabilities are in kcal/mol).*

[4] M. Lindqvist, K. Borre, K. Axenov, B. Kótai, M. Nieger, M. Leskelä, I. Pápai, T. Repo, *J. Am. Chem. Soc.*, **2015**, *137*, 4038.

2.6. Sn/N based FLPs as hydrogenation catalysts [12-14]

The Lewis acid components used in FLP-catalyzed hydrogenation reactions are predominantly triarylboranes BAr_3, particularly $B(C_6F_5)_3$ and similar derivatives. Recently, the range of Lewis acids displaying FLP-like reactivity has expanded to encompass a number of other main-group compounds, of which Sn-centered Lewis acids were shown to be readily accessible and inexpensive alternatives to boranes. We initiated a new collaboration in our project with the Ashley group (Imperial College London), which aimed at exploring the reactivity of Sn/N based FLPs.

The historically important Lappert stannylene $[(Me_3Si)_2CH]_2Sn$, which can acts as both a Lewis base and Lewis acid, is a paradigm system for investigating oxidative addition reactions using a low-valent main-group centre, yet its reactivity with H_2 has been unexplored. This compound was shown to activate H_2 in conjunction with a range of amine bases, forming the previously unreported dihydride $[(Me_3Si)_2CH]_2SnH_2$ species [12]. Kinetic measurements and computational studies point to frustrated Lewis pair mechanism, which involves very unusual late transition state of H_2 activation. When the coordinating base DBU was used, H_2 activation was observed to be reversible, which remains extremely rare for oxidative addition/reductive elimination at main group centers. DFT calculations reveal that the reactions proceed via initial H_2 heterolysis leading to a tight ion pair intermediates, which then rapidly rearrange structurally and deliver the proton to the Sn centre (Figure 10). This polar mechanism could be supported by kinetic isotope effect measurements.

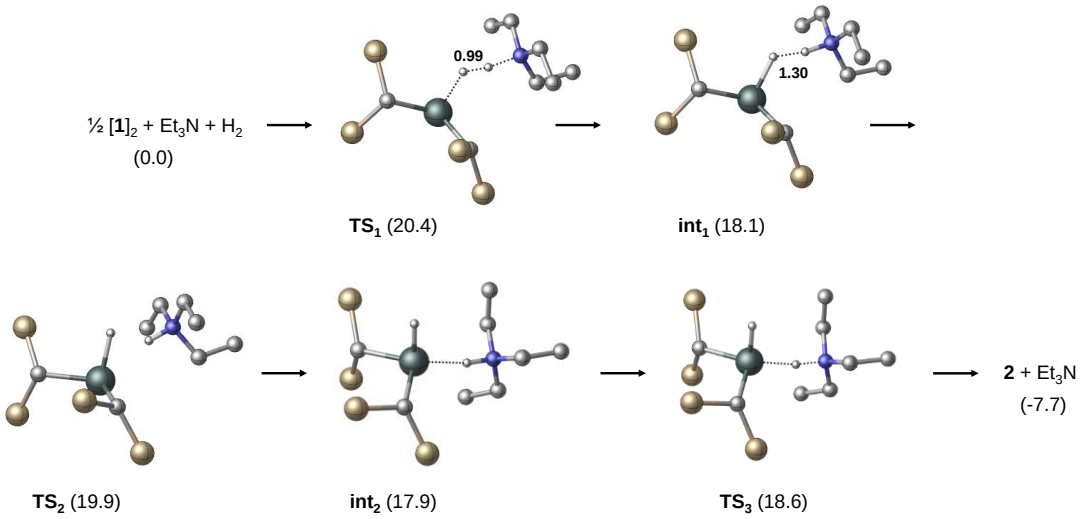


Figure 10: *Mechanism revealed from computations for the reaction of Lappert stannylene with H_2 acting NEt_3 as a base catalyst (relative stabilities are in kcal/mol). The methyl groups of the Me_3Si units are omitted for clarity.*

Cationic Lewis acids are gaining interest as targets for FLP mediated catalysis. Unlike neutral boranes, the Lewis acidity of cations can be tuned through modulation of the counteranion, however detailed studies on such anion effects are currently lacking in the literature. A joint experimental-computational mechanistic study was undertaken for H_2 splitting reaction with $^iPr_3SnOTf$/base pairs [13]. DFT calculations carried out for base = quinuclidine (qui) case indicated that the ground state of this system involves a complex equilibrium between various species (qui[**Sn**]OTf, [**Sn**]OTf + qui, [**Sn**]qui$^+$ + OTf^-, [**Sn**]$(OTf)_2^-$; [**Sn**] = $^iPr_3Sn$), which greatly affects the barrier of H_2 splitting (Figure 11). These species were characterized experimentally as well via $^{119}Sn\{^1H\}$ NMR measurements. The calculation have also revealed that on the product side of the reaction, species with strong H-bonding interaction such as quiH$^+$...qui provide notable stabilization. The experimental observation regarding the low conversion of the H_2 activation process could be rationalized based on the predicted free energy data. Our work highlighted the importance of how the counteranion (OTf^- in this case) can impact the reactivity of cationic Lewis acids beyond a simple modulation of acidity, and we anticipate that these findings will translate to the reactivity of other systems.

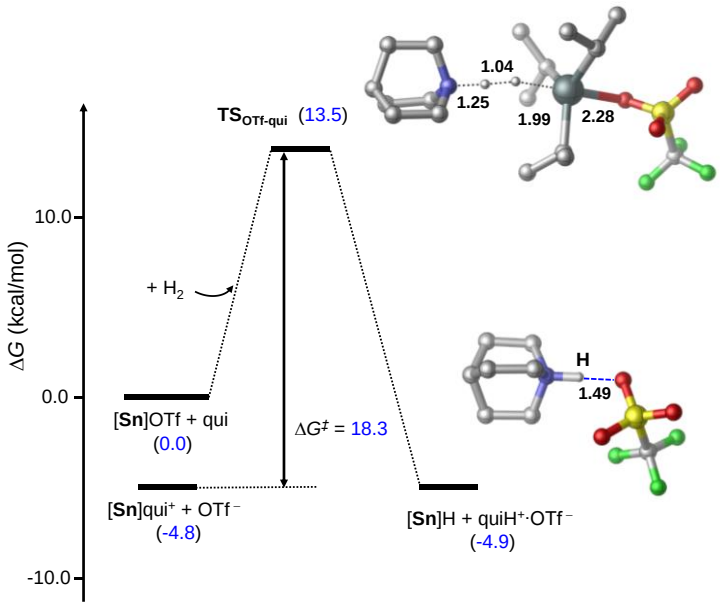


Figure 11: *H_2 activation with the [**Sn**]OTf/qui pair. Relative stabilities (in kcal/mol) are with respect to the most favored reactant state ([**Sn**]qui$^+$ + OTf$^-$).*

In a follow-up work, we examined the mechanistic details of direct hydrogenation of various esters to alcohols catalyzed by the [**Sn**]NTf_2/lutidine frustrated Lewis pair [14]. Examples of main-group-catalyzed hydrogenation of esters are rare, hence the observed transformation warranted a detailed mechanistic investigation. DFT calculations showed that the introduction of NTf_2^- anion increased the Lewis acidity of the tin-centre, leading to a more facile H_2 cleavage compared to that with the previously investigated [**Sn**]OTf_2. In order to garner insight into the stark reactivity differences found between the reduction of CF_3CO_2Et and CH_3CO_2Et, DFT calculations were performed to predict the most feasible pathways mediated by [**Sn**]OTf_2 (Figure 12).

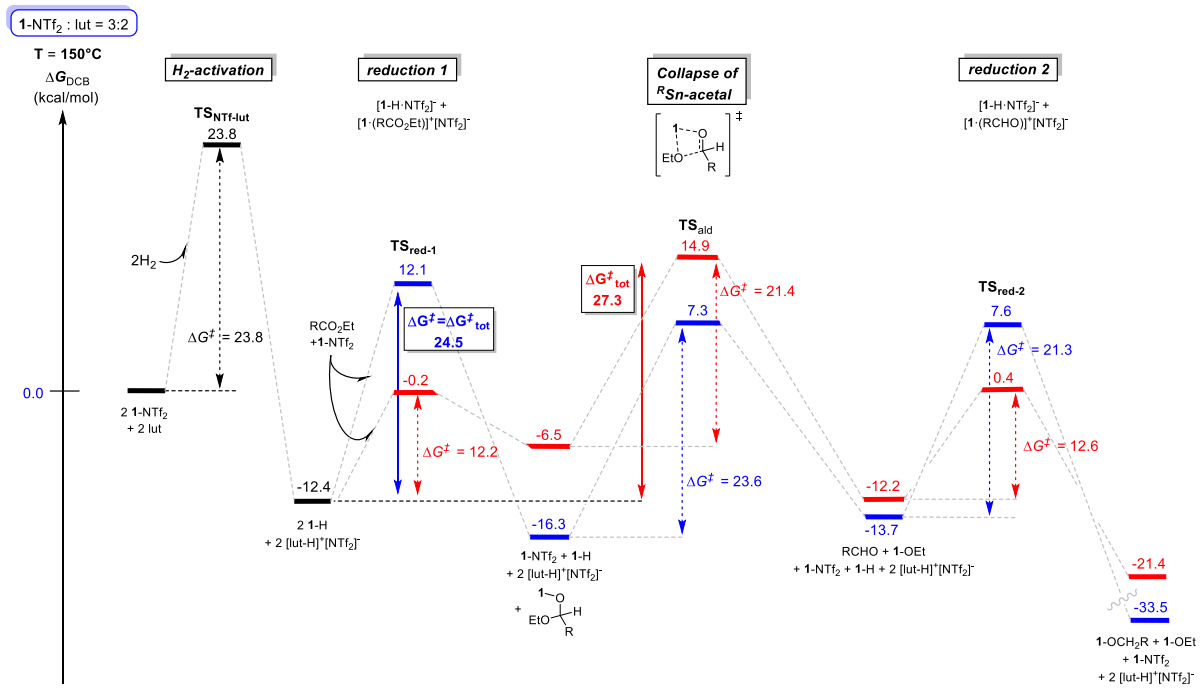


Figure 12: *Mechanism of ester reduction as revealed by DFT calculations. Comparison of esters RCO_2Et (R = CH_3, red; R = CF_3, blue). Relative stabilities are given in kcal/mol.*

The reaction commences with H_2 activation by the lut/**1**-NTf_2 pair, and the reduction ester involves several steps: (i) pre-activation of the ester through complexation of **1**-NTf_2; (ii) subsequent hydride attack on C=O via transition state $\mathbf{TS}_{\mathbf{red\text{-}1}}$; (iii) elimination of **1**-OEt via $\mathbf{TS}_{\mathbf{ald}}$ to produce aldehyde RCHO; (iv) activation of RCHO by **1**-NTf_2; (v) reduction via $\mathbf{TS}_{\mathbf{red\text{-}2}}$ to yield the Sn-alkoxides **1**-OCH_2R and **1**-OEt. Despite the similarity of the elementary steps for both esters, key energetic differences are found in the relative stabilities of intermediates and transition states that account for the reactivity trend. This collaboration was a testimony that computational and experimental work fruitfully supplement one another, leading to such mechanistic details that would otherwise be unattainable.

3. Summary

The primary goal of the present project was to gain basic mechanistic understanding on the exceptional reactivity of sterically hindered Lewis acid/base pairs (frustrated Lewis pairs – FLPs), and utilize this knowledge in catalyst development. We used various tools of computational chemistry to identify the factors that determine the reactivity and selectivity in FLP-mediated H-H and C-H activation processes. Computational analysis assisted in fine-tuning the acid/base properties of FLPs such as simple triaryl-borane/base pairs and *ortho*-phenylene linked aminoboranes, and provided new insight into mechanism of FLP-induced borylation reactions. The origin of stereoinduction in direct hydrogenation of imines catalyzed by chiral boranes could be revealed computationally, which lead to the development of a new catalyst that improved the enantioselectivity. Computational studies highlighted the importance of counteranions in modulating the reactivity of cationic Sn-centered Lewis acids in hydrogenation processes. The previously proposed simple reactivity model of FLP-mediated H_2 cleavage was shown to be valid in a finite temperature dynamic picture as well.

Publications following the order of citations

[1] Zhivonitko V, Sorochkina K, Chernichenko K, Kótai B, Földes T, Pápai I, Telkki V-V, Repo T, Koptyug IV: *Nuclear Spin Hyperpolarization with ansa-Aminoboranes: A Metal-Free Perspective for Parahydrogen-Induced Polarization*, ***Phys. Chem. Chem. Phys.***, *18*, 27784-27795, **2016**.

[2] Chernichenko K, Kótai B, Nieger M, Heikkinen S, Pápai I, Repo T: *Replacing C_6F_5 groups with Cl and H atoms in frustrated Lewis pairs: H_2 additions and catalytic hydrogenations*, ***Dalton Trans.***, *46*, 2263-2269, **2017**.

[3] Chernichenko K, Lindqvist M, Kótai M, Nieger M, Sorochkina K, Pápai I, Repo T: *Metal-Free sp^2-C–H Borylation as a Common Reactivity Pattern of Frustrated 2-Aminophenylboranes*, ***J. Am. Chem. Soc.***, *138*, 4860–4868, **2016**.

[4] Iashin V, Chernichenko K, Pápai I, Repo T: *Atom-Efficient Synthesis of Alkynylfluoroborates Using BF_3-Based Frustrated Lewis Pairs*, ***Angew. Chem. Int. Ed.***, *55*, 14146–14150, **2016**.

[5] Iashin V, Berta D, Chernichenko K, Nieger M, Moslova K, Pápai I, Repo TJ: *Metal-free C-H borylation of N-heteroarenes by boron trifluoride*, ***Chem. Eur. J.***, *26*, 13873-13879, **2020**.

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