Hydrogen Activation

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Expanding the Scope of Metal-Free Catalytic Hydrogenation through Frustrated Lewis Pair Design**

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The further development of the field of catalysis is based on the discovery, understanding, and implementation of novel activation modes that allow unprecedented transformations and open new perspectives in synthetic chemistry. In this context, the recently introduced concept of frustrated Lewis pair (FLP) from the Stephan research group represents a fundamental and novel strategy to develop catalysts based on main-group elements for small-molecule activation.[1] These sterically encumbered Lewis acid–base systems are not able to form a stable donor–acceptor adduct, nevertheless, an intermolecular association of the Lewis acidic (LA) and basic (LB) components to a unique "frustrated complex" was proposed.[2,3] Our research group has also shown that this encounter pair cleaves hydrogen in a cooperative manner and the steric congestion implies a strain, which can be directly utilized for bond activation.[2]

Using steric hindrance as a critical design element, several combinations of bulky Lewis acid–base pairs were effectively probed for heterolytic cleavage of hydrogen.[4–6] Moreover, this remarkable capacity of FLPs was exploited in metal-free hydrogenation procedures.[7] Additionally, the bifunctional and unquenched nature of the FLPs makes them capable of reacting with alkenes,[8] dienes,[9] acetylenes,[10] and THF.[5f] Although this type of reactivity represents a breakthrough in main-group chemistry, its enhanced and non-orthogonal nature obviously limits the synthetic applicability of FLPs. Herein we report an attempt to develop frustrated Lewis pairs with orthogonal reactivity and improved functional-group tolerance for catalytic metal-free hydrogenation.

The previously reported FLP-based hydrogen activation relied mostly on tris(pentafluorophenyl)borane[11] (**1**) as the LA component.[12] Because of the hard-type Lewis acidity of boron in **1** and its inactivation by common oxygen- and/or nitrogen-containing molecules, careful substrate design was needed for successful catalytic hydrogenation reactions. This synthetic limitation triggered us to develop FLP catalysts that have a broader range of applications and possible selectivity in reduction processes.

Our design concept for increased functional-group tolerance is based on the simple hypothesis that steric hindrance in FLPs is a relative phenomenon (Figure 1): further increase of

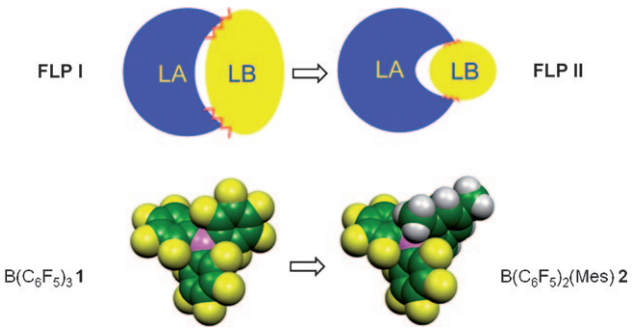

Figure 1. Strategy to develop FLP catalysts with enhanced functional-group tolerance.

congestion around the boron center in **FLP I** and its parallel decrease around the LB could lead to a Lewis pair (**FLP II**) that may have a markedly higher tolerance for the functionalities of common organic molecules. Thus, the steric demands imposed on the boron center by additional *ortho*-aryl substituents are such that they can prevent or markedly decrease the complexation ability with normal Lewis bases but still allow the cleavage of the small hydrogen molecule. Additionally, we assumed that the increased shielding around boron in **FLP II** could preclude its addition to olefins, therefore creating a unique opportunity to investigate the chemoselectivity of FLP-catalyzed hydrogenations.

In an effort to realize this concept, we selected mesityl borane $B(C_6F_5)_2(Mes)$ (**2**)[13] as a possible bulky Lewis acid for an improved FLP catalyst for hydrogenation (Figure 1; Mes = mesityl = 2,4,6-trimethylphenyl).[14] The methyl groups render the boron center not only less accessible but also less electrophilic, which results in a lower intrinsic Lewis acidity than that of perfluorinated borane **1**. Furthermore, the steric factors are also expected to lower the Lewis acidity, because the *ortho*-methyl groups engender further increase of the front and back strain[15] during the complexation of Lewis bases with the boron center. Nevertheless, owing to the steric dependence of the front strain, one would assume to exploit sufficiently high overall Lewis acidity to affect heterolytic hydrogen splitting.

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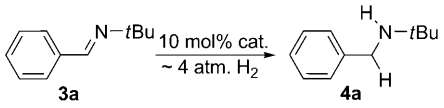
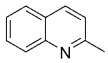
Besides the optimization of the LA component, we wished to apply commercially available amines as possible LB components. By combining these sterically and electronically different amines with borane **2**, we began to explore their applicability in metal-free FLP hydrogenation (Table 1). The objectives of these investigations were twofold: 1) to test the capacity of these novel FLPs in the hydrogen-splitting reaction and 2) to document that the formed ammonium hydridoborate can reduce the imine functionality of substrate **3a**.[16] Aliphatic amines **5**–**9** (Table 1, entries 1–5) with varying steric demand were first evaluated for a possible catalytic process. The primary amine **5** afforded a donor–acceptor complex according to the chemical shift observed in its ^{10}B NMR spectrum (Table 1, entry 1), and this complex was not able to catalyze the hydrogenation of **3a** at ambient temperature. In contrast, the combination of bulkier amines **6**–**9** with borane **2** established an equilibrium, which is shifted toward non complexed LA/LB pairs (Table 1, entries 2–5) according to the NMR studies.[17] However, these systems proved to be poor catalysts in the model reaction.

Table 1: Investigation of Lewis pairs in catalytic metal-free hydrogenation of imine **3a**.[a]

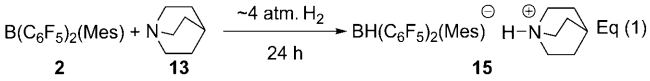


Entry	Lewis base (LB)		δ_{10B} [ppm][b]	Yield [%][c]
1	**5**		−4.3[d]	0
2	**6**		70.5	5
3	**7**		70.1[e]	0
4	**8**		70.1	2
5	**9**		68.3	2
6	**10**		0.5	2
7	**11**		68.1	3
8	**12**		69.3	1
9	**13**		67.8	48
10	**14**		66.1	100

[a] All reactions were performed with **3a** (1 mmol), 10 mol% **2** and added amine **5**–**14** in 0.75 mL of [D$_6$]benzene under an atmosphere of H_2 ($\approx$4 atm) at ambient temperature. [b] ^{10}B NMR measurements were carried out in [D$_8$]toluene at −25 °C, the predicted amount of the major component is over 95%. [c] Yields were determined by GC analysis. [d] The Lewis adduct crystallized out slowly. [e] Color was observed as a result of the presumed α-hydride abstraction as side reaction.

Next, we evaluated the sterically more accessible, planar quinoline-type bases **10**–**12**. Despite the dative complex formation, quinoline (**10**) was able to promote the hydrogenation (Table 1, entry 6). When applying pairs of borane **2** and bulkier, slightly more basic quinoline derivatives **11**, **12**, however, no improvement in the catalytic performance was observed (Table 1, entries 7 and 8). Finally, the utilization of small, but relatively basic amines, such as quinuclidine (**13**) and DABCO (**14**), gave encouraging results (Table 1, entries 9 and 10).[18] In particular, using the less basic DABCO gave full conversion of imine **3a** into amine **4a** at ambient temperature (Table 1, entry 10).

In situ NMR investigations of hydrogen-splitting reactions were carried out for selected **2**/LB pairs.[19] The exposure of a solution of the **2**/**13** pair in [D$_5$]bromobenzene to an atmosphere of H_2 ($\approx$4 atm) resulted in the formation of the presumed ammonium hydridoborate [Eq. (1)]. The obtained chemical shift of $\delta = -22.1$ ppm in the ^{10}B NMR spectrum is comparable to that of the related [HB(C$_6$F$_5$)$_3$][4a] and [HB(C$_6$F$_4$H)$_3$][4f] systems ($\delta = -25.5$ and −23.7 ppm, respectively). Moreover, the resonances from the ^{19}F NMR spectrum are consistent with the formation of a tetracoordinate anionic



borate.[17] Finally, the ^{1}H NMR spectra featured a diagnostic resonance of H−B at $\delta = 3.89$ ppm with a $^1J(^{11}B\text{-}^1H)$ coupling of 107 Hz.[17] These data are consistent with formulation of **15** as [CH(CH$_2$CH$_2$)$_3$NH]$^+$ [HB(C$_6$F$_5$)$_2$(Mes)]$^-$.

In parallel to their catalytic performance, the **2**/**8** and **2**/**13** pairs showed significant differences in the hydrogen-splitting capacity during in situ NMR experiments. Although **2**/**8** could achieve only 10% conversion after 1 hour, the **2**/**13** pair could reach 60% conversion in the same time.[17]

The above results highlight the importance of the dual structural and electronic optimization of both LA and LB components to attain efficient FLP catalysts, and also support the validity of the original design framework. However, the principle illustrated in Figure 1 embodies a dilemma concerning the reaction mechanism of hydrogen splitting. The question is whether the diminished contact area between the bulky Lewis acid **2** and "tiny" bases (e.g. **13** or **14**) is still enough to form the presumed encounter pair (the frustrated complex). In other words, whether the attractive intermolecular interactions can ensure the requisite spatiotemporality,[20] definable time and distance parameters, for the proposed cooperative cleavage of hydrogen to be operative.[2]

To address this quandary, and rationalize the base-dependence of reactivity, we performed quantum chemical calculations for the **2**/**13** + H_2 and **2**/**8** + H_2 systems.[21] It was reassuring to find that weakly bound complexes with preorganized active centers can be identified for both FLPs, and the interaction energies of the most stable forms (−8.4 and

−7.6 kcal mol^{-1} for the **2**/**13** and **2**/**8** pairs, respectively) are similar to previously studied systems.[2,3f,i,6a] Nevertheless, the size difference between the bases has remarkable effects, as apparent from the potential energy curves with respect to the B···N distance (Figure 2).

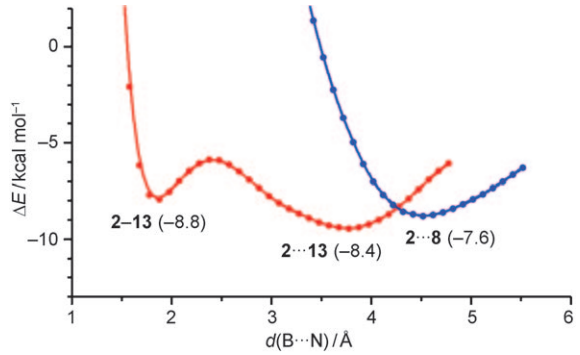


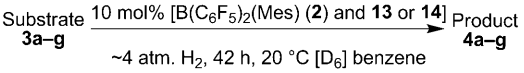
Figure 2. Potential energy curves computed at the M05-2X/6-31G* level for the interaction of **2** with bases **13** and **8**. Interaction energies at the minima calculated at the M05-2X/6-311++G** level are shown in parentheses.

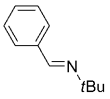
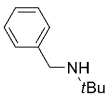
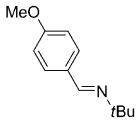
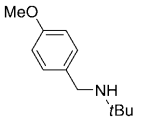
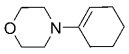
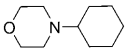
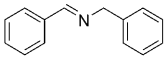
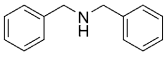
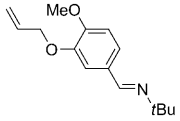
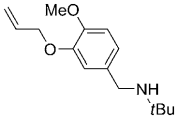
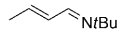
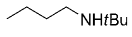
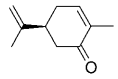
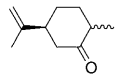
The small quinuclidine base (**13**) affords favorable interaction with **2** in a broad *d*(B···N) range, and even the datively bound **2**···**13** complex can be identified on the potential energy surface with binding energy comparable to that of **2**···**13**. In contrast, the intermolecular interaction already becomes repulsive at a rather large B···N distance in **2**···**8**, which may hamper efficient cooperative base→σ*(H_2) and σ(H_2)→borane donations, which is identified as a key feature for the unique reactivity of FLPs. We indeed found, in accordance with experiments, that the transition state located for the heterolytic hydrogen splitting with **2**/**8** lies higher in energy than that of the **2**/**13** + H_2 reaction (at 0.0 and −2.2 kcal mol^{-1} with respect to the **2** + LB + H_2 level).[22,23]

Having identified the most efficient LA/LB combinations for metal-free hydrogenation, we investigated their scope, functional-group tolerance, and possible selectivity (Table 2). First, we chose substrates which were already studied in metal-free hydrogenations using intramolecular FLP systems (Table 2, entries 1–4).[5d,7b] The results obtained demonstrate that the novel intermolecular FLP catalysts (**2**/**13** and **2**/**14**) show the expected functional-group tolerance. Not only the methoxy functionality was tolerated (Table 2, entry 2), but also the sterically less demanding enamine **3c** and benzyl imine **3d** underwent hydrogenation, although the efficiency of these processes was LB dependent (Table 2, entries 3 and 4).

Next, the hydrogenation of the more challenging allyloxy substrate **3e** was studied (Table 2, entry 5). Similarly to the imines **3a**,**b**, a smooth reduction to the secondary amine **4e** took place. Most importantly, neither cleavage of the allyl group nor the FLP addition to the double bond occurred. Additionally, the reduction of the non-activated double bond was not observed during the reaction. In an attempt to achieve chemoselective hydrogenation, the reduction of

Table 2: Hydrogenation of selected substrates to evaluate functional-group tolerance and selectivity of FLP catalysts **2**/**13** or **2**/**14**.[a]



Entry	Substrate	Yield with **13** [%]	Yield with **14** [%]	Products
1	**3a** 	81	100[b]	**4a** 
2	**3b** 	75	98	**4b** 
3	**3c** 	73	92	**4c** 
4	**3d** 	49	16	**4d** 
5	**3e** 	72	100	**4e** 
6	**3f** 	97	24 (33)[c]	**4f** 
7	**3g** 	n.d.[d,e]	87[d,f]	**4g** 

[a] Yield was determined by ^{1}H NMR analysis (average of two experiments). [b] Reaction time was 24 h instead of 42 h. [c] The yield of butyraldimine as a partially saturated intermediate is given in parentheses. [d] Used 20 mol% of catalyst the reaction time was 6 days. The yield was determined by GC analysis. [e] The polymerization of the product occurred. [f] Diastereomeric ratio is 4.3:1 (*trans*/*cis*). n.d. = not determined.

crotyl imine **3f** was examined, but both imine and activated double bond functionalities were saturated in the case of FLP **2**/**13** catalyst (Table 2, entry 6). However, the efficiency of the processes again depends on the basicity of the LB constituent. Using the less efficient **2**/**14** pair, not only the reaction rate decreased but also the presence of an intermediate with a saturated olefinic bond could be detected.[20] Finally, the reduction of carvone (**3g**) was probed because it is a frequently studied test reaction in transition-metal based catalytic hydrogenation methods (Table 2, entry 7).[24] Contrary to the conventional palladium and platinum-catalyzed hydrogenation, the FLP catalyst **2**/**14** could selectively reduce the activated olefinic bonds and afforded dihydrocarvone (**4f**), thus illustrating the power and potential of FLP-catalyzed hydrogenation. It is also remarkable that neither olefin migration nor terminal olefin saturation was observed. It seems plausible that the steric demands around the C=O bonds in the substrates dictates the chemoselectivity of this metal-free hydrogenation.

In summary, based on a conceptual framework, we have developed unique frustrated Lewis acid–base catalytic systems with unprecedented orthogonal reactivity. Moreover, we identified intermolecular FLP catalysts in which the efficiency of the hydrogen activation was dictated by the steric effects.

Aside from orthogonal reactivity, we have also demonstrated that chemoselectivity can be achieved in catalytic metal-free hydrogenations. Efforts to broaden the scope of the above concept and FLP systems are underway and will be reported in due course.

Experimental Section

General procedure for the catalytic metal-free hydrogenation employing FLP Systems (**2** with **13** or **14**): In a glovebox, substrate (**3a**–**g**, 1 mmol), $B(C_6F_5)_2(Mes)$ (**2**, 50 mg, 0.10 mmol, 10 mol%), quinuclidine (**13**, 12 mg, 0.10 mmol, 10 mol%) or DABCO (**14**, 12 mg, 0.10 mmol, 10 mol%), and dry [D_6]benzene (0.75 mL) were placed into a 55 mL Schlenk bomb equipped with a small magnetic stirrer bar. The Schlenk bomb was then attached to a double manifold H_2/vacuum line and degassed (freeze-pump-thaw cycle × 3). The reaction mixture was cooled in liquid N_2 and 1 atm of H_2 was introduced. The flask was sealed and warmed up to RT. The reaction mixture was then stirred at 500 rpm, at 20 °C, where the initial H_2 pressure is ≈4 atm. After 42 h the yield was determined by ^{1}H NMR or GC analysis.

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[17] See the Supporting Information.

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[22] The free-energy barriers computed with respect to the isolated reactants reflect the same trend (see the Supporting Information).

[23] The relative basicities of **13** and **8** cannot account for the difference in reactivity towards H_2: calculated proton-attachment energies are 243.6 and 243.5 kcal mol^{-1}, respectively.

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