Accepted Manuscript

Correlating electronic and catalytic properties of frustrated Lewis pairs for imine hydrogenation

Éva Dorkó, Bianka Kótai, Tamás Földes, Ádám Gyömöre, Imre Pápai, Tibor Soós

PII: S0022-328X(17)30269-3

DOI: 10.1016/j.jorganchem.2017.04.031

Reference: JOM 19918

To appear in: Journal of Organometallic Chemistry

Received Date: 21 February 2017

Revised Date: 21 April 2017

Accepted Date: 25 April 2017

Please cite this article as: É. Dorkó, B. Kótai, Tamá. Földes, Áá. Gyömöre, I. Pápai, T. Soós, Correlating electronic and catalytic properties of frustrated Lewis pairs for imine hydrogenation, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2017.04.031.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.





Trends in Hydride ion affinity Gutmann-Beckett method Catalytic FLP hydrogenation of imine was compared -F₀-F₃

Correlating Electronic and Catalytic Properties of Frustrated Lewis Pairs for Imine Hydrogenation

Éva Dorkó, Bianka Kótai, Tamás Földes, Ádám Gyömöre, Imre Pápai,* and Tibor Soós*

Research Centre for Natural Sciences, Hungarian Academy of Sciences, Institute of Organic Chemistry, Magyar tudósok körútja 2, H-1117 Budapest, Hungary. *Corresponding author: <u>soos.tibor@ttk.mta.hu</u>, <u>papai.imre@ttk.mta.hu</u>

Keywords: Lewis acidity, frustrated Lewis pairs, DFT, hydrogenation, catalysis

Dedicated to Prof. John A. Gladysz on his 65th birthday.

Introduction

The recently introduced concept of frustrated Lewis pair (FLP) [1] has become a fundamental strategy to develop main-group-element-based catalysis. An FLP is composed of a sterically overcrowded Lewis acid (LA) and a Lewis base (LB) that are unable to form a dative complex because of steric hindrance. As a result, a highly reactive and cooperative Lewis acidbase pairs evolve that can promote various unprecedented reactions, among which the heterolytic activation of hydrogen excels. This remarkable capacity has been exploited in metal-free hydrogenation in which onium (phosphonium, ammonium, etc.) borohydrides are generated to reduce multiple bonds [2, 3, 4] such as of imines, enamines, carbonyls, silyl ethers and α,β -enones.

The diverse reactivity of FLPs has often rendered them incompatible with many common functionalities and solvents, therefore the success of the FLP hydrogenation hinges on the selection of Lewis acidic and basic components. While the identity of the basic component can influence certain catalytic behavior, the primary challenge is to select the right Lewis acidic component for FLP hydrogenation. Therefore, methods to analyze and quantify the impact of steric and electronic properties of Lewis acids on their reactivity are needed to make a rational and informed decision upon FLP catalyst development. Along this line, the goal of the present study is to fine-tune the electronic properties of boron-based Lewis acids and identify trends across them that could accelerate the FLP catalyst development for imine hydro-

genation. Therefore, a series of boranes with default sterical setting has been synthesized and their electronic properties were systematically varied and evaluated by various methods.

Previous efforts in our group have focused on the development of designer FLPs to increase further the practicality of FLP hydrogenation. Using a deliberate structural design on boronbased Lewis-acids, the size-exclusion design, we could secure orthogonal FLP reactivity in hydrogenation, improve the functional group tolerance and even render FLP hydrogenation of carbonyls moisture tolerant [5]. Given the success of FLPs with size-exclusion design we were interested to fine-tune the electronic properties of this type of catalysts for a given target of interest, for an imine reduction. Therefore two series of boranes having a general BX_2Y structure have been targeted, where Y refers to an aryl-ring having minimum two chlorines or methyl groups in ortho positions and X refers to the aryl-rings with minimum two ortho fluo-rine substituents. Accordingly, the steric congestion around the boron atom is a default and practically the same as chlorine atom and methyl group are isosteric. Additionally, variation of substituents in the *meta* and *para* positions of X or Y aryl rings allows to gauge the impact of the electronic effect on Lewis acidity and reactivity.

The first series of triaryl-boranes has a mesityl- and two fluorophenyl-rings and twelve different boranes were envisioned (**Scheme 1**) [6, 7]. The mesityl-rings were chlorinated in the *meta*-positions gradually (the non-chlorinated mesityl derivatives designated as **1**, monochlorinated **2**, dichlorinated **3**), and the fluorinated rings were changed systematically from 2,6difluorophenyl (**a**, F2) to 2,3,6-trifluorophenyl- (**b**, F3), 2,3,5,6-tetrafluorophenyl- (**c**, F4) and perfluorinated-rings (**d**, F5). A second series of triaryl-boranes was also targeted (**4a-c**, **5b-c**, **Scheme 1**). These boranes have a chlorinated phenyl group (the 2,6-dichlorophenyl-ring was designated as **4**, 2,3,6-trichlorophenyl-ring as **5**) and F2-F4 fluorinated fluorophenyl-rings (**a**– **c**). It is important to note, that some of this borane variant have been successfully used for reduction of carbonyls [5].



Scheme 1. In the labelling, numbers refer to the chlorinated rings (1: mesityl-, 2: 3-chloromesityl-, 3: 3,5dichloromesityl-, 4: 2,6-dichlorophenyl-, 5: 2,3,6-trichloroophenyl-ring) and the letters to fluorinated rings (a: 2,6-difluorophenyl, b: 2,3,6-trifluorophenyl, c: 2,3,5,6-tetrafluorophenyl-, d: perfluorinated-ring). (two column

wide)

Results and discussion

The synthesis of mesityl-boranes was performed in three steps and based on the protocol we have previously developed and reported [6, 7]. To generate a BX₂Y type of borane library, potassium mesityltrifluoroborate salts (**7a-c**) were selected as synthetic intermediates (**Scheme 2**). Thus, bromomesityl-compounds (**6a-c**) were treated with *n*-butyllithium or activated magnesium, and then reacted with trimethylborate. The reaction was quenched with hydrochloric acid, and the resulted boronic acid was treated with KHF₂. It is worth noting that these mesityl-fluoroborates **7a-c** are easily available by this method in larger scale. Finally, Grignard reagent (fluorophenyl-magnesiumbromide, **9a-d**) was prepared from the appropriate 1-bromofluorobenzenes (**8a-d**, for details, see SI). Next, two equivalent of these Grignard reagent (**9a-d**) was added dropwise to a suspension of one equivalent of corresponding mesityl-gl-BF₃K salts (**7a-c**) in ether type solvent at 0°C. After work-up, the desired boranes (**1a-3d**) could be isolated in serviceable 31-86% yields as white solids in 5-10 g scale. The ¹H and ¹⁹F NMR data clearly indicated that the aryl rings in boranes can rotate freely; the signals were sharp and well separated at room temperature.



Scheme 2: Preparation of mesitylboranes (for 6a, 7a: $R^1=R^2=H$; for 6b, 7b: $R^1=Cl$, $R^2=H$; for 6c, 7c: $R^1=R^2=Cl$) (1.5 column wide)

Evaluation of Lewis acidity

After having these boranes **1–5** in hand, we embarked on the evaluation of the impact of electronic properties on their acidity. However, unlike Brønsted acidity, the quantitative measurement of Lewis acidity is more complicated because the Lewis acidity is situation dependent (e.g. it is affected by the steric demand of a Lewis base) [8, 9, 10]. Nevertheless, several methods have been developed to evaluate and rank Lewis acids. Methods include Gutmann's acceptor numbers (AN) [11, 12], Drago, Marks, and Wayland's equations [13, 14], Childs-Marks scale [15], and Christe and co-worker's fluoride affinities [16], and Evanseck's method [17]. Alternatively, the calculated hydride affinities are also considered as a reasonable measure for the acidic strength, especially when Lewis acid catalysts are developed for FLP mediated hydrogenation [18, 19, 20].

First, the Lewis acidity of boranes **1-5** was examined computationally. Density functional theory was applied to compute hydride affinities (HA) defined as the Gibbs free energy of hydride detachment from LA-hydride complex anions. The calculations were carried out using the B3LYP-D3 functional, and implicit solvent models with different polarity (toluene, chloroform, dichloromethane) were tested to estimate the solvent effect [21].

The computed gas-phase HAs of the examined boranes are depicted in **Figure 1** as a function of the number of F atoms in the X aryl rings. The obtained results reveal a systematic trend as expected from the electronic nature of the F, Cl and CH₃ aryl substituents. For instance, the HA increases gradually with the number of fluorines. The effect is clearly more enhanced for H/F substitutions at the *meta*-positions as compared to the *para*-substitution. Boranes with chlorinated phenyl substituents show larger HAs, than the corresponding mesityl analogues. The reduced acidity of mesityl-boranes is related to electron donation from the methyl groups. In both phenyl- and mesityl-boranes, H/Cl substitution increases HA by a few kcal/mol.



Figure 1. Gasphase HAs of $B(C_6F_xH_{5-x})_2Y$ boranes (x: number of fluorine atoms on the two equivalent phenyl rings). (one column wide)

Solvent effects are found to have a notable influence on the relative hydride affinities as illustrated in **Figure 2**. Although the acidity trend with respect to the number of F substituents remains very similar, the electronic effect of Cl substitution is not strictly apparent. This could be partially associated with the fact that the hydride affinity values vary in a narrower energy range as the polarity of solvent increases (see **Figure 3**). In addition, polar solvents such as dichloromethane tend to reduce the stability of mesityl-borohydrides as compared to the phenyl analogues, so these two series of boranes are well separated in the diagram shown in **Figure 2**.



Figure 2. HA-s of $B(C_6F_xH_{5-x})_2Y$ boranes in DCM solvent, where x is the number of fluorines on the two equivalent phenyl rings. (one column wide)



Figure 3. Relative hydride ion affinities for the $B(C_6F_xH_{5-x})_2Mes$ series compared to **1a** ($B(C_6F_2H_3)_2Mes$) in gasphase and toluene, chloroform, dichloromethane solvents. (one column wide)

For characterization of Lewis acid 1–5, the Gutmann-Beckett method was chosen, thus the change in the ³¹P NMR chemical shift ($\Delta\delta$) was measured between free Et₃PO and that of the Et₃PO-Lewis acid adduct in CD₂Cl₂. The $\Delta\delta$ values of the prepared boranes 1–5 were analyzed with respect to B(C₆F₅)₃, which is the archetypal Lewis acid of the FLP chemistry. The chemical shift of the dative complex of Et₃PO-B(C₆F₅)₃ was considered as 100% on this acidity scale and 0% was the δ value of the free Et₃PO base.



Figure 4. Relative Lewis acidity of $B(C_6F_xH_{5-x})_2Y$ boranes *via* Gutmann-Beckett method, measured with Et₃PO in CD₂Cl₂, where x is the number of fluorines on the two equivalent phenyl rings. (one column wide)

To explore the consequence of successive replacement of hydrogen with F or Cl, the relative Lewis acidities of 1-5 were measured in CD₂Cl₂ solvent using the Gutmann-Beckett method (Figure 4). Most importantly, unlike the computed hydride affinity (Figure 2), a nonlinear trend has been established by the Gutmann-Beckett method that can be rationalized by the enhanced steric congestions around the boron center when complexed with Et₃PO. For mesityl-series 1-3, the data indicates that the meta-chlorine substituents on the mesityl ring has only a minor impact on the Lewis acidity in case of F4- and F5-rings, similar to the trend found in HA (Figure 1 and 2), but has an affect in the case of F3-ring. For F2-ring derivatives, an anomaly was observed in the relative Lewis-acid strength; the most chlorinated compound 3a (Cl₂MesF₂) somehow appeared to be the weakest acid in the 1a-3a series. As the Gutmann-Beckett method can only gauge the relative acidities of complexed boranes, in case of very weak dative complexes the obtained data might be less appropriate for comparisons. Interestingly, the acidity values were almost the same for the chloromesityl (2b-d) and dichloromesityl (3b-d) rings. These data suggest that the electronic tuning of the bulkier aromatic rings (Y vs X) has a lower impact on Lewis acidity. As the sterically overcrowded aryl rings (Y) are enforced to be perpendicular to the plan of three *ipso*-C atoms, there is a lower level of conjugation with the boron center, which presumably results in the observed trend. For the chlorophenyl series 4–5, the variation of relative Lewis acidity is proved to be negligible. Additionally, the hydride ion affinity predicts that the chlorophenyl-series 4-5 well separate from the mesityl series 1-3, however, in the Gutmann-Beckett method, the obtained Lewis acidity values of the mesityl and chlorophenyl series appear to be much closer.

The above study indicates that even Et_3PO can exert such a steric repulsion upon dative adduct formation with sterically overcrowded boranes **1–5**, that the Lewis acid scale is significantly perturbed. The contribution of this steric effect upon dative bond formation (the facialstrain) was then demonstrated by applying a more bulky Lewis base, such as Ph₃PO. When this sterically hindered base was applied as a reference base for Gutmann-Beckett method, significantly larger differences in relative acidities of the boranes could be observed (**Figure 6**).



Figure 6. Lewis acidity of $B(C_6F_xH_{5-x})_2Y$ boranes *via* Gutmann-Beckett method, measured with Ph₃PO in CD₂Cl₂, where x is the number of fluorines on the two equivalent phenyl rings. (one column wide)

Hydrogenation experiments

To compare the Lewis acidity and hydrogenation capacity of boranes **1–5**, all boranes were evaluated in the same benchmark reaction. The test reaction was the reduction of *N*-benzylidene-*tert*-butylamine to *N*-benzyl-*tert*-butylamine, in benzene solvent, with DABCO, as the LB (Scheme 3).



Scheme 3. The benchmark reaction for borane reactivity evaluation (one column wide)

Most importantly, all borane/DABCO pairs were effective catalysts for reduction of *N*-benzylidene-*tert*-butylamine (Table 1). Data also indicates that chlorophenyl boranes **4–5** have higher catalytic capacity compared to mesityl boranes **1–3**, since conversions were com-

plete within 3 hours in presence of **4–5**. This general trend correlates well with the calculated hydride affinity scale in DCM (**Figure 2**.), but shows deviation from trend determined by the Gutmann-Beckett method (**Figure 4**.).

<mark>Entry</mark>	<mark>Catalyst</mark>	Conversion (%) in						
		0.5h	1h	2h	3h	4h	6h	24h
<mark>1</mark>	-	0	0	0	0	0	0	0
<mark>2</mark>	1d	24	32	64	81	87	99	99
<mark>3</mark>	1c	36	43	68	91	99	99	99
<mark>4</mark>	1b	7	10	20	70	87	99	99
<mark>5</mark>	<mark>1a</mark>	1	3	5	6	9	16	48
<mark>6</mark>	<mark>2d</mark>	20	35	48	80	99 —	99	99
<mark>7</mark>	2c	24	42	60	88	99	99	99
<mark>8</mark>	<mark>2b</mark>	9	15	26	40	80	99	99
<mark>9</mark>	<mark>2a</mark>	0	0	3	6	15	21	61
<mark>10</mark>	<mark>3d</mark>	5	12	23	33	43	65	99
<mark>11</mark>	<mark>3c</mark>	6	17	29	38	44	57	99
<mark>12</mark>	<mark>3b</mark>	2	8	11	17	27	50	99
<mark>13</mark>	<mark>3a</mark>	0	0	2	2	3	8	40
<mark>14</mark>	<mark>4c</mark>	53	68	99	99	99	-	-
<mark>15</mark>	<mark>4b</mark>	37	56	75	94	99	-	-
<mark>16</mark>	<mark>4a</mark>	8	20	32	47	56	80	99
<mark>17</mark>	<mark>5c</mark>	32	48	65	99	99	-	-
<mark>18</mark>	<mark>5b</mark>	22	33	57	90	99	-	-

Table1. Conversion of imine in FLP hydrogenation. (two column wide)

For comparison, catalytic conversions to amine after 2 hours were gathered (**Figure 7**). The data indicates that F4-ring containing **1c**, **2c**, **3c** boranes (entries 3, 7, 11) were more effective catalysts for imine reduction than the **1d**, **2d**, **3d** boranes with perfluorophenyl rings (entries 2, 6, 10). However, the Lewis acidity of these boranes was almost identical in both Gutmann-Beckett methods and HA calculations. This discrepancy can be explained by the lower catalyst stability of the F5 series, as they can decompose in an aromatic nucleophilic substitution reaction [7].



Figure 7. Conversions in 2 hours with $B(C_6F_xH_{5-x})_2Y$ boranes as catalysts, where x is the number of fluorines on the two equivalent phenyl rings (one column wide)

In the case of **1a**, **2a**, **3a** F2 series (entries 5, 9, 13) and **1b**, **2b**, **3b** F3 series (entries 4, 8, 12), the catalytic capacities were also in agreement with the calculated hydride ion affinity and Gutmann-Beckett method results. The Lewis acidity trends and the conversions were similar in case of the **1a-d** mesityl and **2a-d** chloromesityl-boranes (entries 2-5 vs 6-9). In case of **3a-d** boranes with dichloromesityl rings, however, the conversions were reduced (entries 10-13), and no full conversion was achieved within 6 hours. Similar behaviour can be seen in the catalytic performance of the **4–5** chlorophenyl boranes, while the Lewis acidities were rather similar according to both hydride ion affinity calculations and Gutmann-Beckett measurements, the reactivity of **5b,c** boranes with trichlorinated rings were markedly lower compared to **4a–c** boranes with dichlorinated rings (entries 14-16 vs 17,18). This might be explained that the hydride donation capacity of the stronger Lewis acids is lower.

Conclusions:

Gradually substituting *meta-* and *para-*hydrogen atoms to fluorines or chlorines, a series of seventeen triaryl-boranes with a general BX_2Y structure was generated for FLP hydrogenation and comprehensively characterized using combined experimental and theoretical methods. As a consequence of structural design, this series of boranes has a default sterical setting around the boron center and their electronic properties were systematically varied. As demonstrated, the Gutmann-Beckett method has a limited capacity to gauge the Lewis acidity of these highly congested Lewis acids and correlate their FLP hydrogenation utility. Nevertheless, this study reveals that the calculated hydride affinity is a useful tool to quantify the elec-

tronic effects on Lewis acidity and predict the hydrogenation capacities of these boranes. As a general trend, the hydrogen-fluorine 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 affecting Lewis acidity and FLP reactivity and can guide future catalyst developments.

Acknowledgements

This work was supported by the National Research, Development and Innovation Office (K-116150 and K-115660).

Appendix A. Supplementary data

All measurement and synthesis data, and information about chemical compounds and computational details are available in SI.

References

[1] G.C. Welch, R.R. San Juan, J.D. Masuda, D.W. Stephan, Reversible, Metal-Free Hydrogen Activation, Science 314 (2006) 1124–1126, doi: 10.1126/science.1134230.

[2] D.W. Stephan, S. Greenberg, T.W. Graham, P. Chase, J.J. Hastie, S.J. Geier, J.M. Farrell, C.C. Brown, Z.M. Heiden, G.C. Welch, M. Ullrich, Metal-Free Catalytic Hydrogenation of Polar Substrates by Frustrated Lewis Pairs, Inorg. Chem. 50 (2011) 12338–12348, doi: 10.1021/ic200663v.

[3] D.W. Stephan, G. Erker, Frustrated Lewis Pair Chemistry: Development and Perspectives, Angew. Chem. Int. Ed. 54 (2015) 6400–6441, doi: 10.1002/anie.201409800.

[4] D.W. Stephan, The Broadening Reach of Frustrated Lewis Pair Chemistry, Science 354 (2016) 1248–1257, doi: 10.1126/science.aaf7229.

[5] Á. Gyömöre, M. Bakos, T. Földes, I. Pápai, A. Domján, T. Soós, Moisture-Tolerant Frustrated Lewis Pair Catalyst for Hydrogenation of Aldehydes and Ketones, ACS Catal. 5 (2015) 5366–5372, doi: 10.1021/acscatal.5b01299.

[6] G. Erős, H. Mehdi, I. Pápai, T. A. Rokob, P. Király, G. Tárkányi, T. Soós, Expanding the Scope of Metal-Free Catalytic Hydrogenation through Frustrated Lewis Pair Design, Angew. Chem. Int. Ed. 49 (2010) 6556–6563, doi: 10.1002/anie.201001518.

[7] G. Erős, K. Nagy, H. Mehdi, I. Pápai, P. Nagy, P. Király, G. Tárkányi, T. Soós, Catalytic Hydrogenation with Frustrated Lewis Pairs: Selectivity Achieved by Size-Exclusion Design of Lewis Acids, Chem. Eur. J. 18 (2012) 574–585, doi: 10.1002/chem.201102438.

[8] Comparative Lewis acidity of halogenated arylboranes: A.E. Ashley, T.J. Herrington, G. G. Wildgoose, H. Zaher, A.L. Thompson, N.H. Rees, T. Krämer, D. O'Hare, Separating Electrophilicity and Lewis Acidity: The Synthesis, Characterization, and Electrochemistry of the Electron Deficient *Tris*(aryl)boranes $B(C_6F_5)_{3-n}(C_6Cl_5)_n$ (n = 1-3), J. Am. Chem. Soc. 133 (2011) 14727–1474, doi: 10.1021/ja205037t.

[9] M.M. Morgan, A.J.V. Marwitz, W.E. Piers, M. Parvez, Comparative Lewis Acidity in Fluoroarylboranes: $B(o-HC_6F_4)_3$, $B(p-HC_6F_4)_3$, and $B(C_6F_5)_3$, Organometallics 32 (2013) 317–322, doi: 10.1021/om3011195.

[10] B.L. Durfey, T.M. Gilbert, Computational Studies of Lewis Acidities of *Tris*(fluorophenyl)-Substituted Boranes: An Additive Relationship Between Lewis Acidity and Fluorine Position, Inorg. Chem. 50 (2011) 7871–7879, doi: 10.1021/ic201182p.

[11] U. Mayer, V. Gutmann, W. Gerger, The Acceptor Number - a Quantitative Empirical Parameter for the Electrophilic Properties of solvents, Monats. Chem. 106 (1975) 1235–1257, doi: 10.1007/BF00913599.

[12] M.A. Beckett, G.C. Strickland, J.R. Holland, K.S. Varma, A Convenient N.M.R. Method for the Measurement of Lewis Acidity at Boron Centres: Correlation of Reaction Rates of Lewis Acid Initiated Epoxide Polymerizations with Lewis acidity, Polymer 37 (1996) 4629–4631. doi: 10.1016/0032-3861(96)00323-0.

[13] R.S. Drago, B.B. Wayland, A Double-Scale Equation for Correlating Enthalpies of Lewis Acid-Base Interactions, J. Am. Chem. Soc. 87 (1965) 3571–3577, doi: 10.1021/ja01094a008.

[14] A.P. Marks, R.S. Drago, Prediction and Correlation of the Enthalpies of Gas-Phase Ionic Reactions, Inorg. Chem. 15 (1976) 1800–1807, doi: 10.1021/ic50162a013.

[15] R.F. Childs, D.L. Mulholland, A. Nixon, The Lewis Acid Complexes of α , β -unsaturated Carbonyl and Nitrile Compounds. A nuclear magnetic resonance study, Can. J. Chem. 60 (1982) 801–808, doi: 10.1139/v82-117.

[16] K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson, J. A. Sheehy, J. A. Boatz, On a Quantitative Scale for Lewis Acidity and Recent Progress in Polynitrogen Chemistry, J. Fluorine Chem. 101 (2000) 151–153, doi: 10.1016/S0022-1139(99)00151-7.

[17] J.A. Plumley, J.D. Evanseck, Trends and Index of Boron Lewis Acidity, J. Phys. Chem. A 113 (2009) 5985–5992, doi: 10.1021/jp811202c.

[18] T.A. Rokob, A. Hamza, I. Pápai, Rationalizing the Reactivity of Frustrated Lewis Pairs: Thermodynamics of H_2 Activation and the Role of Acid–Base Properties, J. Am. Chem. Soc. 131 (2009) 10701–10710, doi: 10.1021/ja903878z.

[19] T.A. Rokob, I. Pápai, Hydrogen Activation by Frustrated Lewis Pairs: Insights from Computational Studies, Top. Curr. Chem. 332 (2013) 157–212, doi: 10.1007/128_2012_399.

[20] Z.M. Heiden, A.P. Lathem, Establishing the Hydride Donor Abilities of Main Group Hydrides, Organometallics 34 (2015) 1818–1827, doi: 10.1021/om5011512.

[21] For computational details, see Supporting Information.

Highlights

- 1. Combined computational and experimental work to probe Lewis acidity of some sterically highly congested boranes to be used in FLP hydrogenation.
- 2. Gutmann-Beckett method of estimating Lewis acidity has limited capacity for these bulky boranes.
- 3. Calculated hydride affinity represents a more appropriate parameter for gauging Lewis acidity and correlate their FLP hydrogenation utility.

Chillip Mark