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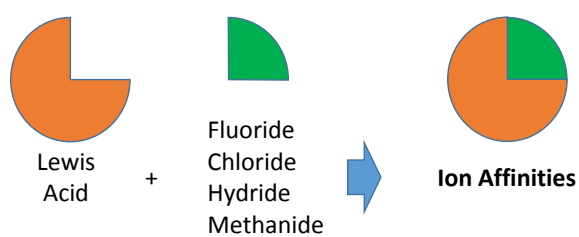
## From unsuccessful H<sub>2</sub>-Activation with FLPs containing B(Ohfp)<sub>3</sub> to a systematic evaluation of the Lewis Acidity of 33 Lewis Acids based on Fluoride, Chloride, Hydride and Methyl Ion Affinities.

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**Keywords:** Frustrated Lewis Pairs – Hydrogen – Lewis Acidity – Ion Affinities – Quantum Chemical Calculations.

TOC Graphic and Short Text



**From Hard to Soft:** The ion affinities of large set of 33 Lewis acids towards hard and soft bases were examined with a unified isodesmic approach and benchmarked for a smaller subset in ccSD(t)/DZ->QZ quality.

### Abstract

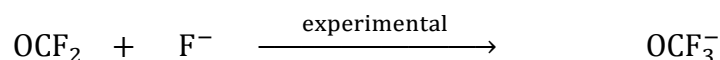
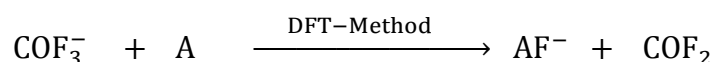
The possibility to obtain frustrated Lewis pairs (FLPs) suitable for H<sub>2</sub>-activation based on the Lewis acid B(Ohfp)<sub>3</sub> **1** (Ohfp = OC(H)(CF<sub>3</sub>)<sub>2</sub>) was investigated. In this context, the crystal structure of **1**, as well as the crystal structure of the very weak adduct **1**·NCMe was determined. When reacting solutions of **1** with H<sub>2</sub> (1 bar) and selected phosphanes, amines, pyridines and N-heterocyclic carbenes, dihydrogen activation was **never** observed. Without H<sub>2</sub>, adduct formation with **1** was observed to be an equilibrium process, regardless of the Lewis base adduct. Thus, the thermodynamics of the H<sub>2</sub> activation of **1** in comparison to the well-known B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was analyzed by DFT calculations in the gas phase and different solvents (CH<sub>2</sub>Cl<sub>2</sub>, *ortho*-difluorbenzene and acetonitrile). These investigations indicated that FLP chemistry based on **1** is considerably less favored than the one with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. This is in

agreement with control NMR experiments indicating hydride transfer from  $[\text{H-B}(\text{Ohfip})_3]^-$  upon reaction with  $\text{B}(\text{C}_6\text{F}_5)_3$  giving  $[\text{H-B}(\text{C}_6\text{F}_5)_3]^-$  and  $\text{B}(\text{Ohfip})_3$  in toluene and also MeCN.

Induced by these unsuccessful reactions, the Lewis acidity towards HSAB hard and soft ions was investigated for a deeper insight. A unified reference system based on the trimethylsilyl compounds  $\text{Me}_3\text{Si-Y}$  ( $\text{Y} = \text{F}, \text{Cl}, \text{H}, \text{Me}$ ) and their respective ions  $\text{Me}_3\text{Si}^+ / \text{Y}^-$  calculated at the G3 level was chosen as anchor point. The individual ion affinities were then assessed based on subsequent isodesmic reactions calculated at the much less expensive level (RI-)BP86/SV(P). This method was validated by systematic calculations of smaller reference systems at the frozen core CCSD(T) level with correlation effects extrapolated to a full quadruple- $\zeta$  basis. Overall, 33 common and frequently used Lewis acids were ranked with respect to their FIA, CIA, HIA and MIA (fluoride / chloride / hydride / methyl ion affinity).

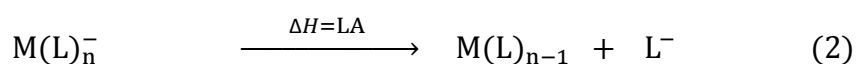
## Introduction

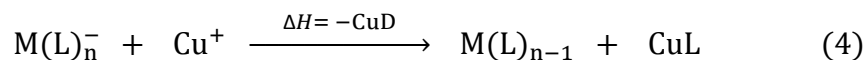
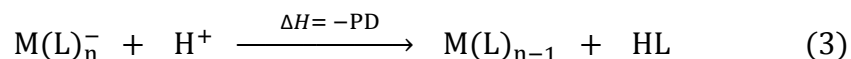
In the past years Lewis acids, and especially their strongest representatives, were of great interest and found applications in catalysis, ionization, rearrangement reactions and bond heterolysis reactions.<sup>[1-6]</sup> Naturally, tabulating the strengths of Lewis acids is very important and useful to estimate the potency of a given Lewis acid. But in contrast to the strength of Brønsted Acids, which are typically measured experimentally and ranked within one homogenous medium on the basis of the well-known pH and  $\text{pK}_a$  scales that can be set absolute by using the correct reference state and anchor points, the strength of Lewis acids depends on the formation of a Lewis acid-base pair.<sup>[7-9]</sup> In this respect Brønsted Acidity is a special case of Lewis acidity, in which only one type of Lewis acid (the proton) interacts with a great variety of Lewis bases free of choice. Thus, it is only possible to determine the absolute strength of a Lewis acid, with respect to a well-defined Lewis base. Towards this aim, in 1984 the fluoride ion affinity (FIA) was introduced by Bartlett et al. to classify the strength of the Lewis acid A by the enthalpy that is released by binding a fluoride ion.<sup>[10]</sup> This concept was continued by many others.<sup>[11-20]</sup> To avoid the problems that appear by the calculation of a “naked fluoride ion”, this approach was improved by using the experimental FIA of  $\text{OCF}_2$  of  $209 \text{ kJ mol}^{-1}$  as an anchor point in a (pseudo-)isodesmic reaction (Eq. 1).<sup>[21]</sup>



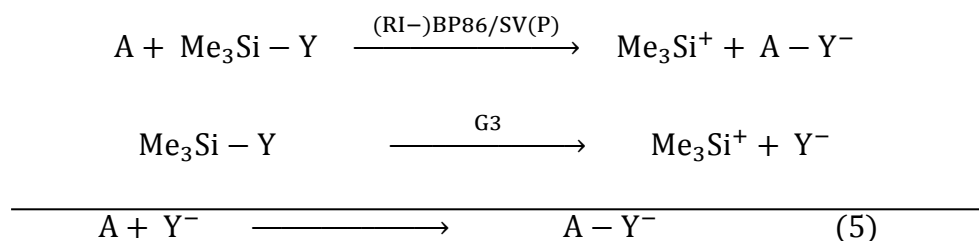
Using this method the strengths of many Lewis acids were classified.<sup>[22]</sup> However, the fluoride ion is a hard base in the HSAB sense,<sup>[23]</sup> so the FIA may be deceptive for HSAB soft Lewis acids. Thus, it is advisable to compare methods with different approaches to find a convenient Lewis acid. Therefore, analogously to the FIA, the affinities to ions of varying hardness (i.e.,  $\text{Cl}^-$ ,  $\text{H}^-$  and  $\text{CH}_3^- = \text{Me}^-$ ) were used to rate the strengths of Lewis acids.<sup>[17, 24, 25]</sup> Unfortunately, there is no consistent reference system, which would allow comparing trends between the different methods and lead to a broadly applicable Lewis acid scale.

However, not only Lewis acids are in the focus of current interest, also weakly coordinating anions (WCAs) have become an indispensable tool in chemistry and found versatile applications. Boron<sup>[26-29]</sup> or aluminum<sup>[30, 31]</sup> based WCAs were used for lithium ion batteries. Other WCAs stabilized reactive cations, e.g.  $[\text{CX}_3]^+$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ),<sup>[14, 32, 33]</sup>  $[\text{P}_n\text{X}_m]^+$  ( $\text{X} = \text{Br}, \text{I}$ ),<sup>[34]</sup>  $[\text{N}_5]^+$ ,<sup>[35]</sup>  $[\text{P}_9]^+$ ,<sup>[36]</sup>  $[\text{AuXe}_4]^{2+}$ ,<sup>[37]</sup>  $[\text{H}(\text{Et}_2\text{O})_2]^+$ ,<sup>[38]</sup>  $[\text{Zn}_2]^{2+}$ ,<sup>[39]</sup> benzidine radical cations,<sup>[40]</sup>  $[\text{Cu}(\text{S}_{12})(\text{S}_8)]^+$ ,<sup>[42]</sup>  $[\text{tBu}_3\text{Si-Ga-SitBu}_3]^+$ ,<sup>[43]</sup> triarylsilylium or -germylium ions,<sup>[44]</sup> protonated benzene,<sup>[45]</sup> and the 2-norbornyl cation.<sup>[46]</sup> Weakly bound complexes like those of ethene with copper,<sup>[48]</sup> silver<sup>[49]</sup> or gold are other examples.<sup>[50]</sup> Ion-like silylium ions coordinated to the carborates<sup>[41]</sup> or the recent  $\text{Me}_3\text{Si-F-Al}(\text{OC}(\text{CF}_3)_3)_3$  present strong Lewis acids.<sup>[47]</sup> Further WCA applications are catalytic C-F activation,<sup>[51]</sup> ionic liquids<sup>[52-58]</sup> and electrochemistry.<sup>[59-67]</sup> Clearly the stability of a typical WCA  $[\text{M}(\text{L})_n]^-$  ( $\text{M} = \text{Lewis acidic central atom of valency } n-1$ ;  $\text{L} = \text{univalent residue}$ ) is related to the strength of the underlying Lewis acid  $\text{M}(\text{L})_{n-1}$ . In earlier work, we judged the relative stabilities of WCAs based on calculations for a representative set of WCAs and their parent Lewis acids.<sup>[18]</sup> They were assessed by the Ligand Affinity (LA), the decomposition in the presence of a hard (proton decomposition PD) and a soft electrophile (copper decomposition CuD), the position of the HOMO, the HOMO-LUMO gap as well as the FIA of the Lewis acid parent to the WCA (Eq. 2-4).





With the current contribution, we augmented the known scale<sup>[18]</sup> for the most common Lewis acids (A) with respect to their CIA (Chloride Ion Affinity), HIA (Hydride Ion Affinity) and MIA (Methyl Ion Affinity) in addition to the FIA. For all XIAs (X = F, C, H, M), we chose a unified reference system. It is based on the trimethylsilyl compounds  $\text{Me}_3\text{SiY}$  (Y = F, Cl, H, Me) and their respective ions calculated at the G3 level as anchor point. Thus, the relative values of the Lewis acidity towards different bases ( $\text{Y}^-$ ) are comparable based on unified reference reactions that were obtained at a highly correlated level, while the residual calculations of the in part very large molecules were assessed based on subsequent isodesmic reactions calculated at a much less expensive level ((RI-)BP86/SV(P)), Eq. 5).



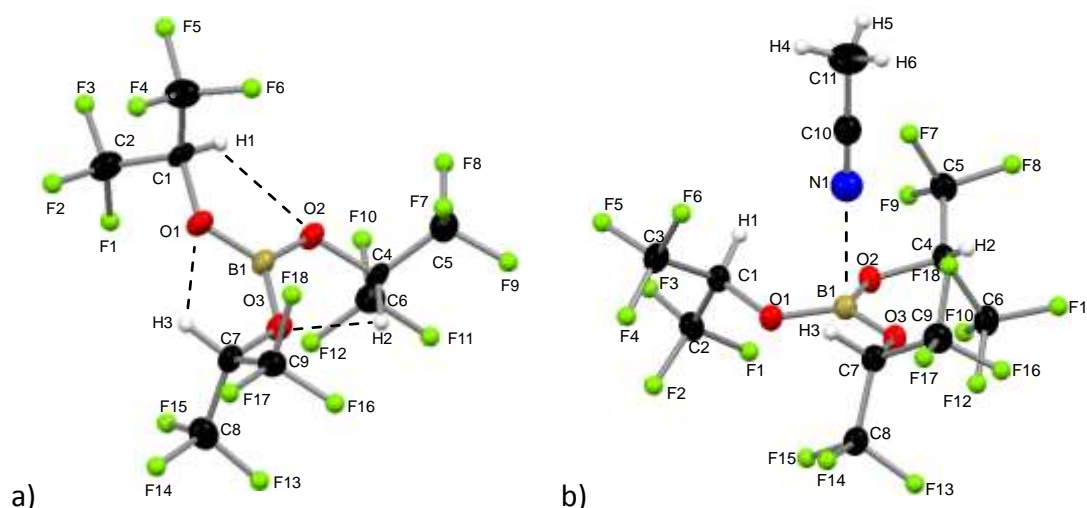
To further validate the data we performed systematic calculations of the smaller reference systems at the frozen core CCSD(T) level with correlation effects extrapolated to a full quadruple- $\zeta$  basis.<sup>[68-71]</sup> The error bar of this methodology was reported to be below  $1 \text{ kJ mol}^{-1}$ ,<sup>[69]</sup> and thus serves as a validation of the simpler isodesmic procedure according to eq. 5 that for size reasons had to be applied for larger Lewis acids. Furthermore, we expanded the known WCA stability scale with the PD and CuD of a series of hitherto not explored WCAs  $[\text{M(L)}_n]^-$ . All calculations were done in the gas phase.

## Results and Discussion

Background of these investigations have been experiments to activate hydrogen with the Lewis acid tris(2H-hexafluoroisopropoxy)borane ( $\text{B}(\text{Ohfip})_3$  **1**), which finds applications in electrochemistry.<sup>[72]</sup> We investigated the possibility to obtain frustrated Lewis Pair (FLP) chemistry<sup>[73]</sup> based on this Lewis acid and reacted it with  $\text{H}_2$  and selected phosphanes, amines and N-heterocyclic carbenes (NHCs), but we have never observed a reaction. Even upon addition of very strong Lewis bases, adduct formation was partly only occurring in

equilibrium. By contrast, the respective anion  $[\text{B}(\text{Ohfip})_4]^-$  is known<sup>[57, 74]</sup> as a rather stable WCA and the FIA of the  $\text{B}(\text{Ohfip})_3$  acid, calculated according to the procedure in eq. 5, is with  $384 \text{ kJ mol}^{-1}$  rather large. Moreover, during the course of the synthesis of  $[\text{B}(\text{Ohfip})_4]^-$  from  $\text{Na}[\text{BH}_4]$  and HO-hfip, the  $[\text{H-B}(\text{Ohfip})_3]^-$  anion is a stable intermediate that needs many hours of reflux to further completely react with HO-hfip to give the symmetric borate. For both reasons, the high FIA of the Lewis acid and the known stability of the  $[\text{H-B}(\text{Ohfip})_3]^-$  anion, we did not expect these unsuccessful reactions and therefore started to perform calculations to investigate and compare the Lewis acidity towards HSAB-different ions for a deeper insight. In the following we first describe our experiments, before turning to the general calculations on a wide set of Lewis acids.

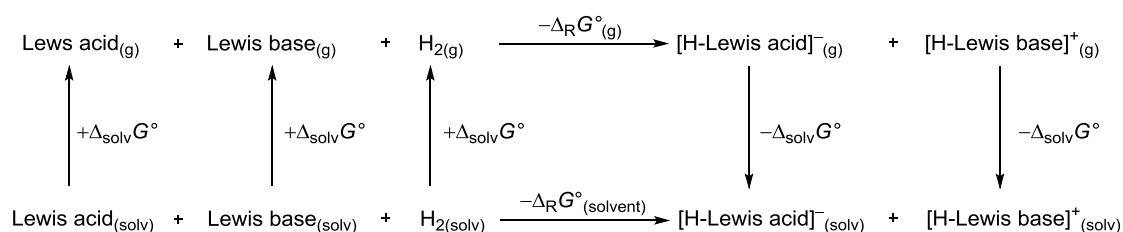
**Synthesis and Characterization:** We synthesized **1** according to the literature and obtained white plate-like crystals melting at  $32^\circ \text{C}$ .<sup>[72]</sup> The Lewis acid **1** crystallizes in the monoclinic space group  $P2_1/c$  and exists, in contrast to the dimeric heavier homologue  $\text{Al}(\text{Ohfip})_3$ , as a monomer.<sup>[75]</sup> The sum of the three O-B-O angles adds up to  $360^\circ$ , so apparently the orbital interactions of the  $\pi$ -system between the boron and oxygen atoms are maximized and the B-O distances of 136 pm are shortened by 11 pm compared to the distances in the THF adduct of  $\text{Na}[\text{B}(\text{Ohfip})_4]$ .<sup>[57]</sup> The C-O distances are with 141 pm nearly unchanged compared to those of HO-hfip.<sup>[76]</sup> Interestingly, the central  $\text{B}(\text{OCH})_3$  unit resides in a plane. This might be attributed to **i)** the steric demand of the hfip residues and **ii)** the formation of three weak intramolecular (C)-H...O hydrogen bonds ( $d_{\text{HO}} = 198 \text{ pm}$ ). Per ligand one  $\text{CF}_3$ -group is above and the other below this central plane. From a multitude of crystallization experiments with a great variety of neutral Lewis bases, we obtained one very weak adduct by dissolving **1** in acetonitrile (**1·NCMe**) and cooling the solution slowly down to  $-40^\circ \text{C}$ . The compound **1·NCMe** crystallizes in the trigonal space group  $R3c$ . To the best of our knowledge we report the longest distance between boron and a nitrogen atom of an acetonitrile molecule (248 pm, Figure 1).



**Fig. 1:** Molecular structures of **1** and **1·NCMe**, thermal ellipsoids are shown at the 50 % probability level. Fluorine atoms are drawn as spheres of arbitrary radius for clarity. Selected distances [pm] and angles [°]: (**1**): B1-O1 = 136.0(4), B1-O2 = 135.8(4), B1-O3 = 135.9(4), O1-C1 = 141.6(3), O2-C2 = 141.6(3), O3-C3 = 141.1(3), O1-H1 = 198.1, O2-H2 = 198.0, O3-H3 = 197.8, O1-B1-O2 = 120.5(3), O2-B1-O3 = 119.7(3), O1-B1-O3 = 119.8(3), B1-O1-C1 = 122.3(2), B1-O2-C4 = 121.7(2), B1-O3-C7 = 122.3(2); (**1·NCMe**): B1-N1 = 248.4, B1-O1 = 136.97(9), O1-C1 = 140.46(16), O1-H1 = 197.0, N1-H1 = 299.4, O1-B1-O2 = 119.57(3), B1-O1-C1 = 121.31(9).

We were rather astonished to see this weak interaction, as the boron nitrogen distances in related complexes like MeCN·BCl<sub>3</sub>, MeCN·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or the acetonitrile adduct of the perfluoroaryldiborane C<sub>6</sub>F<sub>4</sub>-1,2-(B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>)<sub>2</sub> are 156, 162 and 161 pm.<sup>[77-79]</sup> The boron atoms of these complexes are distorted tetrahedrally coordinated. The hitherto longest boron nitrogen distance was measured in the mixed crystal MeCN·(B(CH<sub>2</sub>Ph)<sub>3</sub>)<sub>0.92</sub>(Ga(CH<sub>2</sub>Ph)<sub>3</sub>)<sub>0.08</sub> and amounts to 178 pm.<sup>[80]</sup> The O-B-O angles in **1·NCMe** amount on average to 119.6° and add up to 358.7°, which signals an almost ideal trigonal planar geometry. The averaged B-O bond length is 137 pm and hence only very slightly widened compared to **1** (136 pm). The acetonitrile molecule of **1·NCMe** lies on a pseudo C<sub>3</sub> axis.

**FLP Chemistry:** We continued our investigation by testing the ability of **1** to activate hydrogen with different FLP compounds. To analyze the thermodynamics of the hydrogen activation of **1** in comparison to the well-known B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> the standard Gibbs energies were calculated in the gas phase and different solvents (COSMO solvation model) by using a Born-Fajans-Haber cycle (Figure 2, Table 1).



**Figure 2:** Born-Haber-Fajans cycle to access  $\Delta_R G^0_{(g)}$  and  $\Delta_R G^0_{(solvent)}$  of **1** and  $B(C_6F_5)_3$  in various solvents.

**Table 1:**  $\Delta_R G^0_{(g)}$  and  $\Delta_R G^0_{(solvent)}$  of the  $H_2$ -activation of selected Lewis acid/base-pairs in various solvents (BP86/SV(P)) and calculated according to the cycle in Fig. 2; NHC = 1,3-dimethyl-4,5-diphenyl imidazole-2-ylidene, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene.

<b>Vs. 1</b>	$\Delta_R G^0_{(g)}$	$\Delta_R G^0(CH_2Cl_2)$	$\Delta_R G^0(o\text{-difluoro-benzene})$	$\Delta_R G^0(MeCN)$
<b>Lewis Base</b>				
PMePh <sub>2</sub>	474	341	332	324
P <sup>t</sup> Bu <sub>3</sub>	464	191	174	155
NEt <sub>3</sub>	420	132	114	94
2,6-Lutidine	475	148	127	113
NHPh <sub>2</sub>	480	162	141	120
NHC	313	167	158	163
IDipp	310	53	37	3
<b>Vs. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub></b>	$\Delta_R G^0_{(g)}$	$\Delta_R G^0(CH_2Cl_2)$	$\Delta_R G^0(o\text{-difluoro-benzene})$	$\Delta_R G^0(MeCN)$
<b>Lewis Base</b>				
PMePh <sub>2</sub>	305	196	188	181
P <sup>t</sup> Bu <sub>3</sub>	292	54	39	22
NEt <sub>3</sub>	247	-5	-21	-39
2,6-Lutidine	308	25	6	-14
NHPh <sub>2</sub>	384	273	266	259
NHC	140	30	23	15
IDipp	137	-84	-98	-114

In agreement with our futile experimental efforts, Table 1 shows that FLP chemistry based on **1** is considerably less favored than the one with  $B(C_6F_5)_3$ . Furthermore, these investigations suggested that polar solvents promote  $H_2$  activation and therefore acetonitrile was *inter alia* selected as a solvent. However, we have to point out that even the very weak adduct formation in **1**·MeCN might shut down FLP chemistry. To cope with this concern, we have done several test reactions also in chlorinated solvents like  $CH_2Cl_2$  and did not observe any desired chemistry with  $H_2$  but noted that the liquid  $B(OHfip)_3$  forms two immiscible phases in  $CH_2Cl_2$ . Thus, the investigations were discarded and we concentrated on MeCN, despite its problems. To obtain an experimental confirmation of the relative HIA of the two boron Lewis acids  $B(OHfip)_3$  and  $B(C_6F_5)_3$ , we did react  $K^+[HB(OHfip)_3]^-$  with  $B(C_6F_5)_3$  and expected to get neutral  $B(OHfip)_3$  and  $K^+[HB(C_6F_5)_3]^-$ . This isodesmic reaction was calculated by (RI-)BP86/SV(P) to be exothermic ( $-135 \text{ kJ mol}^{-1}$ ) and exergonic ( $-149 \text{ kJ mol}^{-1}$ ) in the gas phase, in agreement with our expectation from Table 1. Our NMR scale experiments in



MeCN and deuterated toluene confirmed the results of the calculations. After the addition of  $K^+[HB(OHfip)_3]^-$  to a solution of  $B(C_6F_5)_3$  in toluene- $d_8$  immediately a white solid precipitated (mainly  $K^+[HB(C_6F_5)_3]^-$ ). The broad singlet at 17.7 ppm in the  $^{11}B$  NMR spectra of the solution revealed that  $B(OHfip)_3$  had formed, but only a very weak signal of scarcely soluble  $K^+[HB(C_6F_5)_3]^-$  (at around -25 ppm,  $^1J_{H,B} \approx 84$  Hz) and no remaining  $B(C_6F_5)_3$  or  $[HB(OHfip)_3]^-$  was observed. After removing most of the solution with a syringe, deuterated MeCN was added to examine the now soluble precipitate. The  $^{11}B$  NMR spectrum shows mainly the doublet of  $[HB(C_6F_5)_3]^-$  at the typical values  $\delta^{11}B = -25.4$  ( $^1J_{H,B}$  93 Hz). Since it was not possible to get rid of all the solution, still a small signal of  $B(OHfip)_3$  was present in the spectra. It seems, as if a complete conversion takes place in toluene, however, due to the presence of both  $B(OHfip)_3$  and  $[HB(C_6F_5)_3]^-$  in acetonitrile, small amounts of  $[HB(OHfip)_3]^-$  are being formed again. This was backed by the results of the same reaction in acetonitrile instead of toluene, in which the reaction reaches equilibrium, but largely lies on the side of  $[HB(C_6F_5)_3]^-$ . This seems reasonable, since  $B(C_6F_5)_3$  should be less reactive in acetonitrile due to strong adduct formation, while  $B(OHfip)_3$  is only marginally stabilized by MeCN.

**Experiments directed towards FLP-Chemistry:** We started experimental investigations with several common Lewis bases. All following reactions were carried out with argon atmosphere in NMR tubes closed by a J. Young valve according to the following procedure: Compound **1** and the different phosphanes, amines and NHCs were mixed in a 1:1 stoichiometry in  $d^3$ -acetonitrile and characterized by NMR spectroscopy. Subsequently the reaction mixtures were evacuated, exposed to hydrogen pressure of one bar, and were then again NMR spectroscopically analyzed. We started our attempts by using phosphanes, since e.g.  $B(C_6F_5)_3$  **i**) forms an adduct with  $PPh_3$ ,<sup>[81]</sup> **ii**) in combination with  $(C_6F_5)Ph_2P$  it leads to a FLP system capable to reversible activate hydrogen<sup>[82]</sup> and **iii**) a mixture with  $P^tBu_3$  is able to activate terminal alkynes.<sup>[83]</sup> Here  $PPh_3$ ,  $P^tBu_3$  and  $PMePh_2$  did not form classical adducts with **1**, and there is no sign of a hydrogen activation (e.g. doublet  $^1J_{PH}$  in the  $^{31}P$  NMR, doublet  $^1J_{BH}$  splitting in the  $^{11}B$  NMR spectrum: expected for  $[HB(OHfip)_3]^-$  127 Hz at  $\delta = 7.7$  ppm). To eliminate the possibility that the reaction occurs very slowly, in a second approach **1** was stirred with  $PPh_3$  over twenty days and exposed to  $H_2$  at 1 bar, but without any noticeable reaction. Of all the tested bases collected in Table 1, **1** only forms an adduct visible in the NMR with  $NEt_3$ . However, this adduct only exists in equilibrium. Also testing the ability to activate hydrogen failed in all instances. No adduct formation and no hydrogen

cleavage were detected by the combination of **1** and NHPH<sub>2</sub> or 2,6-lutidin, which are able to activate hydrogen in combination with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>[84]</sup> Since it appeared that the reactivity of **1** is not sufficient to activate H<sub>2</sub> with typical Lewis bases like phosphanes and amines, we used the strongly basic NHCs 1,3-dimethyl-4,5-diphenyl-imidazol-2-ylidene and 1,3-di(2,6-diisopropylphenyl)imidazol-2-ylidene. They form classical adducts with **1**, which were observed in the <sup>11</sup>B NMR spectra at 0.8 / 1.3 ppm, but no detectable hydrogen activation occurred.

To investigate, if the Li<sup>+</sup> salt of the [HB(Ohfp)<sub>3</sub>]<sup>-</sup> anion and a protonated Lewis base like [HNEt<sub>3</sub>]<sup>+</sup>Cl<sup>-</sup> are compatible, we dissolved both salts in acetonitrile, and tested, if they are compatible in solution or if they release elemental hydrogen. However, even after stirring for one week, no gas formation occurred and the NMR signals remained unchanged. Thus, no regeneration of the original Lewis acid/Base pairs occurred. The formation of LiCl was never observed in these reactions and it appears that either the salts dissolve as tight ion pairs with no chance for ion exchange (unlikely in polar MeCN), or that the small amounts of LiCl remain metastable as [LiCl(Donor)<sub>x</sub>]<sub>y</sub> aggregates in solution. Overall, we have to note that H<sub>2</sub> activation might still be possible with this system, e.g. with bulkier NHCs as well as HD gas to look for scrambling and H<sub>2</sub> formation in the <sup>1</sup>H NMR spectrum, but at least not with our tested reaction conditions.

### Quantum Chemical Investigations

**Ion Affinities of Lewis acids A:** Earlier and the following calculations to determine ion affinities are based on isodesmic reactions (eq. 1 and 5) with the BP86 functional<sup>[85-87]</sup> and the SV(P) basis,<sup>[88]</sup> which represent a good agreement between costs and accuracy. This method allows fast access to large molecules, which cannot be calculated at correlated levels. Basis reaction of the respective ion affinity calculations were the ion affinities of Me<sub>3</sub>Si<sup>+</sup> against Y<sup>-</sup> giving Me<sub>3</sub>SiY (Y = F, Cl, H, Me), which were calculated at the reliable G3 level (Table 2).

**Table 2:** Calculated reference reaction values (G3 level) as anchor points to determine FIA, CIA, HIA and MIA values.

Reference systems	$\Delta_r H^0$ [kJ mol <sup>-1</sup> ]
Me <sub>3</sub> Si-F → Me <sub>3</sub> Si <sup>+</sup> + F <sup>-</sup>	+958
Me <sub>3</sub> Si-Cl → Me <sub>3</sub> Si <sup>+</sup> + Cl <sup>-</sup>	+759
Me <sub>3</sub> Si-H → Me <sub>3</sub> Si <sup>+</sup> + H <sup>-</sup>	+959
Me <sub>3</sub> Si-Me → Me <sub>3</sub> Si <sup>+</sup> + Me <sup>-</sup>	+1000

**Validation Study:** During our investigation to improve these scales by unifying the reference system and adding up the CIA, HIA and MIA values, we noticed a larger discrepancy in our earlier published FIA values for  $\text{BI}_3$ ,  $\text{AlCl}_3$  and  $\text{AlI}_3$ .<sup>[22]</sup> To validate and confirm the BP86/SV(P) values, we carried out RI-MP2 structure optimizations with TURBOMOLE<sup>[89, 90]</sup> and def2-QZVPP basis sets<sup>[91]</sup> with corresponding RI-C auxiliary bases for all atoms.<sup>[92]</sup> Based on these structures, gas phase reaction energies were calculated according to Eq. 6 with single point calculations at the CCSD(T)(FC)/double- $\zeta$  level plus an MP2 extrapolation of the correlation energy from double- $\zeta$  to quadruple- $\zeta$  basis sets with Gaussian 09 (ESI, S-Table 1).<sup>[93]</sup>



This approach was published earlier by Klopper et al.<sup>[68, 69]</sup> and has successfully been used by our group to study protonation equilibria.<sup>[7-9]</sup>

**Table 2:** Overview on the CIA, HIA and FIA values [in  $\text{kJ mol}^{-1}$ ] of chosen representative Lewis acids calculated via CCSD(T)(FC)/double- $\zeta$  level plus MP2 extrapolation to quadruple- $\zeta$ . The values in parentheses give the discrepancy to the affinity values calculated via eq. 5 at the BP86/SV(P) level.

Lewis acid	CIA	HIA	FIA
$\text{BF}_3$	151 (5)	297 (-2)	346 (4)
$\text{BCl}_3$	195 (12)	395 (5)	384 (8)
$\text{BBr}_3$	219 (7)	440 (2)	425 (-16)
$\text{AlF}_3$	308 (1)	388 (-36)	482 (11)
$\text{AlCl}_3$	320 (3)	428 (-22)	502 (4)
$\text{AlBr}_3$	324 (-2)	425 (-39)	505 (-5)
$\text{GaF}_3$	319 (14)	444 (-18)	447 (13)
$\text{GaCl}_3$	299 (5)	446 (-19)	429 (-5)
$\text{GaBr}_3$	295 (1)	445 (-24)	426 (-13)
$\text{PF}_5$	165 (-14)	400 (-17)	380 (-17)
$\text{PCl}_5$	179 (2)	468 (-14)	393 (1)
$\text{AsF}_5$	237 (-14)	461 (-24)	434 (4)
$\text{SbF}_5$	333 (-8)	530 [517] <sup>b)</sup> (-32/-13)	495 (2)
$\text{B(CN)}_3$	363 (12)	583 (-3)	540 (-10)
$\text{B(OH)}_3$	<sup>a)</sup>	163 (-7)	208 (4)

<sup>a)</sup> Does not form a complex. <sup>b)</sup>  $[\text{SbF}_5\text{H}]^-$  is not stable and would decompose to  $\text{SbF}_4^- + \text{HF}$ , this value is given in brackets.

The CIA and FIA values in Table 2 agree well with the values calculated by BP86/SV(P), however, some of the values may be off by up to  $17 \text{ kJ mol}^{-1}$ . The BP86/SV(P) HIA values of the boron halides,  $\text{B(CN)}_3$  and  $\text{B(OH)}_3$  nicely suit, since the B-H bond is less polar. Nevertheless, if the central atom is not a second row element, the bond gets more polar or hydridic, so the HIA values may be approximately  $20 \text{ kJ mol}^{-1}$  to high. In order to get better

values we also calculated the HIA values with BP86/SVP with a polarization function at the hydrogen, but those values were even inferior to those calculated with BP86/SV(P). Also orienting BP86/TZVP calculations were inferior to the simple BP86/SV(P) method. Thus, for simplicity and to be applicable for a larger set of compounds, we used the BP86/SV(P) method. Since the discrepancy in the HIA values from the absolute values is always in one direction, the relative HIA values at the simpler BP86/SV(P) level are still suitable for discussion.

**Ion Affinity Scale:** With this cadre of verified data, we calculated the FIA, CIA, HIA and MIA for a large set of 33 Lewis Acids A through a set of isodesmic reactions as given in Eq. 5 and with respect to the ion affinities of  $\text{Me}_3\text{Si}-\text{Y}$  ( $\text{Y} = \text{F}, \text{Cl}, \text{H}, \text{Me}$ ) at the G3 level (Table 4).

The HIA and MIA values of main group III halides (Table 3) follow similar trends and rise for the heavier halogen atoms. If we take a look at the affinity values of  $\text{AlF}_3$  and  $\text{GaF}_3$  there is not such a large difference compared to  $\text{AlF}_3$  and  $\text{BF}_3$ , since aluminum and gallium have nearly the same size and aluminum is just a little bit more electropositive than gallium. However, they distinguish in their affinity values towards soft or hard Lewis bases.  $\text{AlF}_3$  favors the hard fluoride ion, while  $\text{GaF}_3$  prefers softer Lewis bases like  $\text{Me}^-$  or  $\text{H}^-$  anions, which confirms that aluminum trifluoride is harder than gallium trifluoride. Nevertheless, if the halide ligands get heavier, gallium turns out scaled by aluminum, which indicates that the  $\text{GaX}_3$  Lewis acids are more stable and less acidic. This could mean that the overlap of the  $\pi$  orbitals is more pronounced and hence the  $\pi$  back bonding is stronger. Summarized, in this row, the  $\text{AlX}_3$  compounds are the strongest Lewis acids with respect to fluoride and chloride, but towards the hydride ion,  $\text{GaX}_3$  acids are stronger and with respect to the methanide ion similar to the aluminum acids. The CIA and FIA values of  $\text{PF}_5$  and  $\text{PCl}_5$  are quite low and nearly identical, which may be a result of the electrostatic repulsion of the six rather hard halides in the octahedral complexes. For the strongest classical Lewis acid  $\text{SbF}_5$ , two HIA and MIA values are given, since  $[\text{SbF}_5\text{H}]^-$  and  $[\text{SbF}_5\text{Me}]^-$  are not stable and would decompose.

**Table 3:** Overview on the calculated CIA, HIA, FIA and MIA values of representative Lewis Acids.  $[\text{SbF}_5\text{H}]^-$  and  $[\text{SbF}_5\text{Me}]^-$  are less stable and would decompose to  $\text{SbF}_4^- + \text{HF}$  and  $\text{SbF}_4^- + \text{MeF}$ , respectively, this value is given in brackets. TMS-F-Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>3</sub> can be attacked, depending on the nucleophile, at the Si or the Al atom and decomposes either to TMS-Y + F-Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>3</sub> or TMS-F + Y-Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>3</sub>. The value for the nucleophilic attack at the Al atom given in parentheses. [a] The anion containing a B-Y-B bridge is thermodynamically favored. [b] The most stable isomer was used. [c] The experimental crystal structure was used as start geometry.[94] Unstable compounds and values of unstable compounds are given in *italics*.

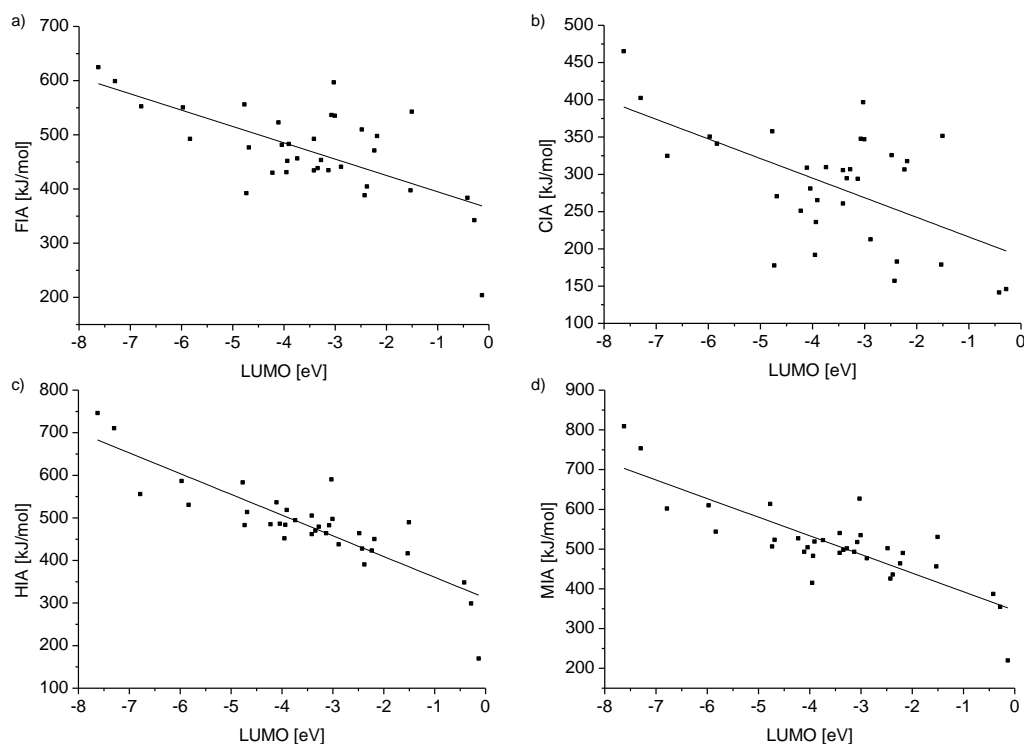
Lewis Acid	LUMO [eV]	CIA [kJ/mol]	HIA [kJ/mol]	FIA [kJ/mol]	MIA [kJ/mol]	Lewis Acid	LUMO [eV]	CIA [kJ/mol]	HIA [kJ/mol]	FIA [kJ/mol]	MIA [kJ/mol]
<b>M-X</b>						B(Ohfip) <sub>3</sub>	-0.42	141	348	384	387
BF <sub>3</sub>	-0.29	146	299	342	355	Al(OC(CF <sub>3</sub> ) <sub>3</sub> ) <sub>3</sub>	-1.51	352	490	543	530
BCl <sub>3</sub>	-2.38	183	391	405	436	B(OTeF <sub>5</sub> ) <sub>3</sub>	-6.78	325	556	552	602
BBr <sub>3</sub>	-2.88	213	438	441	477	As(OTeF <sub>5</sub> ) <sub>5</sub>	-7.30	403	710	559	753
BI <sub>3</sub>	-3.41	261	505	493	540	Sb(OTeF <sub>5</sub> ) <sub>5</sub>	-7.62	465	746	625	809
AlF <sub>3</sub>	-2.24	306	423	471	464	<b>M-C</b>					
AlCl <sub>3</sub>	-2.18	318	450	498	490	B(CN) <sub>3</sub>	-5.97	351	587	551	610
AlBr <sub>3</sub>	-2.48	326	464	510	502	B(CF <sub>3</sub> ) <sub>3</sub>	-4.77	358	583	556	614
AlI <sub>3</sub>	-3.01	347	497	535	535	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	-3.93	236	484	452	483
GaF <sub>3</sub>	-3.41	306	462	434	491	Al(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	-3.07	348	483	536	518
GaCl <sub>3</sub>	-3.13	294	464	434	493	Ga(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	-3.28	307	479	453	502
GaBr <sub>3</sub>	-3.34	295	470	438	498	B(C <sub>12</sub> F <sub>9</sub> ) <sub>3</sub>	-3.95	190	452	431	415
Gal <sub>3</sub>	-3.74	310	495	457	523	B(C <sub>6</sub> H <sub>3</sub> (CF <sub>3</sub> ) <sub>2</sub> ) <sub>3</sub>	-4.04	281	486	482	504
PF <sub>5</sub>	-1.53	179	417	398	456	B(C <sub>10</sub> F <sub>7</sub> ) <sub>3</sub>	-3.91	265	519	483	519
PCl <sub>5</sub>	-4.73	178	483	392	507	F <sub>4</sub> C <sub>6</sub> (1,2-(B(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> ) <sub>2</sub> )	-4.11	309	536 <sup>[a]</sup>	523	493 <sup>[a]</sup>
AsF <sub>5</sub>	-4.22	251	485	430	527	B <sub>2</sub> (C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (C <sub>6</sub> F <sub>4</sub> ) <sub>2</sub>	-4.68	271	514	477	524
SbF <sub>5</sub>	-5.83	341	562 [531]	493	607 [544]	PF <sub>2</sub> (C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub>	-2.42	157 <sup>[b]</sup>	428 <sup>[b]</sup>	388 <sup>[c]</sup>	426 <sup>[b]</sup>
<b>M-O</b>						SiMe <sub>2</sub> CH <sub>2</sub> CB <sub>11</sub> Cl <sub>11</sub>	-3.03	397	590	597	627
B(OH) <sub>3</sub>	-0.13		170	204	220	TMS-F-Al(OC(CF <sub>3</sub> ) <sub>3</sub> ) <sub>3</sub>	-1.21	259 (267)	459 (407)	458	459 (407)

**Putting Boron Acids in Context:** As expected  $B(OH)_3$  is a quite weak Lewis acid and since  $[B(OH)_3Cl]^-$  is experimentally unknown we disregarded this anion from our calculations. Compound **1** reveals relatively low ion affinity values. Compared to  $B(C_6F_5)_3$  the FIA value of **1** is just  $68 \text{ kJ mol}^{-1}$  lower, but the HIA value is  $136 \text{ kJ mol}^{-1}$  lower. This huge difference in the HIA value may explain our experimentally observed results. Similarly, the HIA of  $B(C_6F_5)_3$  is nearly identical with that one of the versus fluoride considerably stronger Lewis Acid  $Al(C_6F_5)_3$ .  $B(C_{12}F_9)_3$  and  $B(C_6H_3(CF_3)_2)_3$  show the same effect, which implies that boron Lewis acids stabilize the hydride ion better than other ions in the corresponding anion. These results are in agreement with HSAB-arguments: **1** and  $Al(C_6F_5)_3$  are considerably harder than the softer boranes with B-C bonds and thus the affinities of the softer boranes are maximal with respect to the softer hydride ions, whereas those of the harder acids are maximal for hard bases like fluoride. The low CIA and FIA, MIA values of  $B(C_{12}F_9)_3$  results from the sterically demanding perfluorinated biphenyl ligands, which hinder the access to the Lewis acid center. Since  $F_4C_6(1,2-(B(C_6F_5)_2)_2)$  has two nearby Lewis acid atoms, small ions like fluoride and hydride prefer a bridged geometry, but the difference between the bridged and not bridged geometry is smaller than  $1 \text{ kJ mol}^{-1}$ .

**Group 14 Acids:** Main group IV is represented by the silylium zwitterion  $SiMe_2CH_2CB_{11}Cl_{11}$ ,<sup>[95]</sup> and the Janus-headed Lewis acid  $TMS-F-Al(OC(CF_3)_3)_3$ .<sup>[47]</sup> The ion affinity of the silylium zwitterion is boosted by around  $140 \text{ kJ mol}^{-1}$  compared to the silicon atom in neutral  $TMS-F-Al(OC(CF_3)_3)_3$ , which itself features IAs only slightly inferior to  $B(C_6F_5)_3$ .

**Lewis Superacids:** Since  $SbF_5$  is viewed as the strongest conventional Lewis acid, the FIA value of monomeric  $SbF_5$  is used to determine Lewis superacids: *“Molecular Lewis acids, which are stronger than monomeric  $SbF_5$  in the gas phase are Lewis superacids.”*<sup>[96]</sup> This approach is simple and since strong Lewis acids and the fluoride anion are typically hard, it gives a nice overview of Lewis acids by their relative strengths. The FIA values of monomeric  $AlCl_3$ ,  $AlBr_3$ ,  $AlI_3$ ,  $Al(OC(CF_3)_3)_3$ ,  $B(OTeF_5)_5$ ,  $As(OTeF_5)_5$ ,  $Sb(OTeF_5)_3$ ,  $B(CN)_3$ ,  $B(CF_3)_3$ ,  $Al(C_6F_5)_3$ ,  $F_4C_6(1,2-(B(C_6F_5)_2)_2)$  and  $SiMe_2CH_2CB_{11}Cl_{11}$  excel the FIA value of  $SbF_5$  and may be classified as Lewis superacids. However, P-based acids like  $PF_2(C_2F_5)_3$  possesses compared to  $PF_5$  slightly lower CIA, FIA and MIA values, due to the steric demand of the  $C_2F_5$  groups in the acid base complexes. The HIA of  $PF_2(C_2F_5)_3$  is a bit higher, since  $H^-$  is small and the steric effect of the  $C_2F_5$  groups is overcompensated by its electron withdrawing effect.

**Relationship between Ion Affinity Values and LUMO level:** To gain a deeper insight in the relationship between the ion affinity values and the LUMO levels of the Lewis acids in Table 3, we plotted the values and added a regression line in each case (see Figure 3).



**Figure 3:** Plots showing the regression lines of the relationships between the ion affinity values and the LUMO level of the Lewis acids collected in Table 3. Linear regression of ion affinity values against the LUMO level for a):  $y = -30.14(6.05)x + 364.61(24.86)$ ,  $R^2 = 0.41$ , b):  $y = -26.31(6.71)x + 189.68(26.85)$ ,  $R^2 = 0.31$ , c):  $y = -48.68(5.06)x + 311.86(19.98)$ ,  $R^2 = 0.73$  and d):  $y = -46.90(5.75)x + 345.77(22.68)$ ,  $R^2 = 0.67$ .

By trend, the gradient shows that a low LUMO level is accompanied with a high ion affinity value. However, a low LUMO level is not automatically connected with a high ion affinity value. Furthermore,  $R^2$  and the value of the gradient of the FIA and CIA values are compared to the corresponding values of the HIA and MIA values significantly smaller. These facts are consistent with Pearson's HSAB concept, since interaction of the soft hydride and methyl ions with Lewis bases are more orbital based and consequently strongly influenced by the LUMO levels. Therefore, the HIA and MIA values are in a distinctive relationship with the LUMO values. Especially the HIA, with significantly less steric influence on the result, can be well predicted by the LUMO level of a given Lewis acid and vice versa. On the other hand, the interaction of the hard fluoride and chloride ions has a high ionic contribution and thus it is less connected to the LUMO energies. At first sight, the FIA would be expected to have an even lower  $R^2$  value than the CIA, because the fluoride ion is harder than the chloride ion. However, the chemistry of fluoride is sometimes exceptional: Since the fluoride atom is

smaller than the chloride, it is possible that the overlapping of the involved orbitals is improved and steric effects are less developed. Therefore, it gets a more covalent character and fits the trend slightly better than chloride.

**Stability of WCAs based on FIA, PD, CuD, HOMO level and HOMO-LUMO gap:** If the before mentioned Lewis acids are expanded by a  $L^-$  ligand, the related WCAs are obtained. We determined the stability towards decomposition, oxidation and reduction for most of the WCAs that relate to the Lewis acids in Table 3. The higher the FIA of the acid, the more stable is the WCA towards ligand abstraction. To rate the stability of a WCA towards attack of a hard ( $H^+$ ) and a soft electrophile ( $Cu^+$ ) the isodesmic decomposition reactions (eq. 2 and 3) were calculated to obtain the proton decomposition (PD) and the copper decomposition (CuD). Herein we show instead of the previously used  $\Delta_r U$  values, the  $\Delta_r G^\circ$  values of the PD and CuD, hence they are closer to laboratory conditions. The entropy  $S$  of the  $H^+$  and  $Cu^+$  cations was calculated by using the Sackur-Tetrode equation.<sup>[97-99]</sup> Since a gaseous anion and a gaseous cation react to give two neutral species, the PD and CuD are both exothermic. The less negative the PD and CuD values are, the more stable is the WCA against electrophilic attack.<sup>[18]</sup> The lower the HOMO energy the more resistant is an anion towards oxidation, hence the electron is harder to remove. The HOMO-LUMO gap is related to its resistance towards reduction. The larger the gap, the more stable is the WCA towards gaining an electron. The data in Table 4 cannot be taken as absolute, but since the same calculation methods were used, relative trends will definitely be correct.



**Table 4:** Calculated properties of WCAs: FIA of the parent Lewis acid as shown in Table 3.

<b>Anion</b> <b>With M-X bonds</b>	<b>FIA</b> <b>[kJ mol<sup>-1</sup>]</b>	<b>PD</b> <b>[kJ /mol<sup>-1</sup>]</b>	<b>CuD</b> <b>[kJ mol<sup>-1</sup>]</b>	<b>HOMO</b> <b>[eV]</b>	<b>Gap</b> <b>[eV]</b>
[BF <sub>4</sub> ] <sup>-</sup>	342	-1212	-540	-1.799	10.820
[BCl <sub>4</sub> ] <sup>-</sup>	405	-1237	-629	-1.708	7.975
[BBr <sub>4</sub> ] <sup>-</sup>	441	-1225	-631	-1.787	5.820
[BI <sub>4</sub> ] <sup>-</sup>	493	-1190	-613	-2.127	3.620
[AlF <sub>4</sub> ] <sup>-</sup>	471	-1083	-411	-2.510	8.016
[AlCl <sub>4</sub> ] <sup>-</sup>	498	-1102	-493	-2.546	7.054
[AlBr <sub>4</sub> ] <sup>-</sup>	510	-1105	-511	-2.505	5.685
[AlI <sub>4</sub> ] <sup>-</sup>	535	-1095	-519	-2.658	3.973
[GaF <sub>4</sub> ] <sup>-</sup>	434	-1118	-446	-2.677	7.048
[GaCl <sub>4</sub> ] <sup>-</sup>	434	-1125	-516	-2.604	5.501
[GaBr <sub>4</sub> ] <sup>-</sup>	438	-1127	-533	-2.532	4.369
[GaI <sub>4</sub> ] <sup>-</sup>	457	-1112	-536	-2.673	3.051
[PF <sub>6</sub> ] <sup>-</sup>	398	-1163	-491	-2.673	8.801
[PCl <sub>6</sub> ] <sup>-</sup>	392	-1242	-633	-2.246	1.929
[AsF <sub>6</sub> ] <sup>-</sup>	430	-1129	-457	-3.150	6.282
[SbF <sub>6</sub> ] <sup>-</sup>	493	-1065	-393	-3.911	5.134
<b>With M-O bonds</b>					
[B(OHfip) <sub>4</sub> ] <sup>-</sup>	384	-1212	-526	-3.377	7.056
[Al(OC(CF <sub>3</sub> ) <sub>3</sub> ) <sub>4</sub> ] <sup>-</sup>	543	-1077	-413	-4.096	6.737
[B(OTeF <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>	552	-1098	-496	-5.547	2.126
[As(OTeF <sub>5</sub> ) <sub>6</sub> ] <sup>-</sup>	559	-1053	-452	-6.129	1.983
[Sb(OTeF <sub>5</sub> ) <sub>6</sub> ] <sup>-</sup>	625	-999	-398	-6.460	2.181
<b>With M-C bonds</b>					
[B(CN) <sub>4</sub> ] <sup>-</sup>	551	-1092	-438	-4.182	6.818
[B(CF <sub>3</sub> ) <sub>4</sub> ] <sup>-</sup>	556	-1143	-411	-3.527	9.069
[B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>	452	-1263	-567	-3.120	4.214
[Al(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>	536	-1224	-528	-3.304	4.251
[Ga(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>	453	-1246	-550	-3.308	4.332
[B(C <sub>12</sub> F <sub>9</sub> ) <sub>4</sub> ] <sup>-</sup>	431	-1231	-534	-3.517	3.339
[B(C <sub>6</sub> H <sub>3</sub> (CF <sub>3</sub> ) <sub>2</sub> ) <sub>4</sub> ] <sup>-</sup>	482	-1250	-527	-3.798	3.930
[B(C <sub>10</sub> F <sub>7</sub> ) <sub>4</sub> ] <sup>-</sup>	483	-1236	-540	-3.098	2.795
[F <sub>4</sub> C <sub>6</sub> (1,2-(B(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> ) <sub>2</sub> )(C <sub>6</sub> F <sub>5</sub> )] <sup>-</sup>	523	-1325	-629	-3.207	1.969
[B <sub>2</sub> (C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (C <sub>6</sub> F <sub>4</sub> ) <sub>2</sub> ] <sup>-</sup>	477	-1259	-563	-3.284	2.548

Among the [MX<sub>4</sub>]<sup>-</sup> anions (M = B, Al, Ga; X = F, Cl, Br, I) the [MF<sub>4</sub>]<sup>-</sup> and [MCl<sub>4</sub>]<sup>-</sup> anions are exceptionally stable towards reduction (see gap), the [MF<sub>4</sub>]<sup>-</sup> and [MI<sub>4</sub>]<sup>-</sup> anions have an increased resistance against an attack of a soft or a hard nucleophile (see PD and CuD). This confirms that especially fluorine is a suitable ligand at the central atom to enhance the properties of a WCA. Usually, the HOMO level rises with increasing weight of the central atoms and ligands. The alkoxyaluminate [Al(OC(CF<sub>3</sub>)<sub>3</sub>)<sub>4</sub>]<sup>-</sup> possesses distinguished thermodynamic stability values paired with a simple straightforward synthesis. Compared to

the teflate based anions it offers similar values (see FIA, PD, CuD, and HOMO level), but it is significant more reduction resistant. These values underline its current role in chemistry to stabilize highly reactive cations.<sup>[14, 33, 38, 39, 42, 43, 48-50, 100, 101]</sup> In addition,

Table 4 includes a series of WCAs with (mainly fluorinated) organic ligands. Of those,  $[\text{B}(\text{CN})_4]^-$  and  $[\text{B}(\text{CF}_3)_4]^-$  offer very good WCA properties, although  $[\text{B}(\text{CF}_3)_4]^-$  allows for additional decomposition pathways.<sup>[102]</sup> Typically, the fluorination of ligands increases the stability values of borate based anions.<sup>[18]</sup> Apart from that, the stability values of all the WCAs including M-C bonds are quite similar.

## Conclusions

Attempts to use the conveniently available  $\text{B}(\text{Ohfip})_3$  as Lewis acid component in FLP chemistry systems failed in our hands for a wide range of neutral Lewis bases and with all used reaction conditions. However, it may well be possible using the right bases (e.g. bulky NHCs), other solvents than MeCN and using HD to study the exchange reactions. To investigate this unexpected result, we introduced and validated a Lewis acid scale based on a consistent reference system ( $\text{Me}_3\text{Si}-\text{Y} / \text{Me}_3\text{Si}^+ / \text{Y}^-$ ;  $\text{Y} = \text{Cl}, \text{H}, \text{F}, \text{Me}$ ). Validation was performed at the highly reliable ccSD(t)/DZ→QZ level for a subset of 15 smaller Lewis acids  $\text{MX}_n$ . These values with an error bar below  $1 \text{ kJ mol}^{-1}$  are the currently best available benchmark calculations on Lewis acidity for these systems. With the consistent reference system and a set of isodesmic reactions, we calculated the CIA, HIA, FIA and MIA values of 33 common and frequently used, partly rather large Lewis acids (Table 3). With this approach, comparable ion affinity values were obtained for four different Lewis bases  $\text{Y}^-$  of differing HSAB hardness. For any given Lewis acid, the consistent ion affinity scale may be extended by performing only five low level calculations and using the herein established reference system. In addition, we evaluated the stability of WCAs that are based on the herein investigated Lewis acids, by calculating their LUMO energies, HOMO-LUMO gap, proton decomposition (PD) and the copper decomposition reaction (CuD). Overall, the reference data collected in this work will be of great help to rationalize experimental findings in all areas of chemistry exploiting Lewis acidity towards hard or soft bases or the selection of a suitable WCA counterion for a given process.

## Experimental Data

**Techniques and Instruments:** All reactions were carried out under an inert atmosphere by using standard vacuum and Schlenk techniques or a glovebox with an argon atmosphere ( $\text{H}_2\text{O}$  and  $\text{O}_2 < 1 \text{ ppm}$ ), Special J. Young NMR tubes sealed with Teflon valves were used to exclude air and moisture. All solvents were dried over  $\text{CaH}_2$  or  $\text{P}_4\text{O}_{10}$  and distilled afterwards.

NMR data were recorded from solutions in  $d^8$ -toluene or  $d^3$ -acetonitrile at room temperature on a BRUKER AVANCE II<sup>+</sup> 400MHz WB spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are given with respect to TMS,  $^{19}\text{F}$  NMR spectra to fluorotrichloromethane,  $^{11}\text{B}$  NMR spectra to the boron-trifluoride-diethyl-ether-complex,  $^{31}\text{P}$  NMR spectra to a 85 % phosphoric(V) acid solution and  $^7\text{Li}$  NMR spectra to 9.7 M LiCl in  $\text{D}_2\text{O}$ . Data collections for X-ray structure determinations were performed on a Rigaku Spider image plate system or a BRUKER APEX II Quazar CCD diffractometer at 100 and 110 K, respectively, with Mo radiation. The single crystals were mounted in perfluoroether oil on a MiTeGen Micromount<sup>TM</sup>.  $\text{B}(\text{Ohfp})_3$  has a the CCSD deposition number 1004582 and the MeCN-adduct 1004583.

**Supporting Information:** Experimental procedures and spectroscopic data are included with the supporting information, as well are detailed energies, vibrational frequencies, xyz-coordinates, solvation energy calculations, HOMO-LUMO-gaps and other data on the computations (>700 pages).

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