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From unsuccessful H₂-activation with FLPs containing B(Ohfp)₃ 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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The possibility of obtaining frustrated Lewis pairs (FLPs) suitable for H₂-activation based on the Lewis acid B(Ohfp)₃ **1** (Ohfp = OC(H)(CF₃)₂) 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 H₂ (1 bar) and selected phosphanes, amines, pyridines and N-heterocyclic carbenes, dihydrogen activation was never observed. Without H₂, adduct formation with **1** was observed to be an equilibrium process, regardless of the Lewis base adduct. Thus, the thermodynamics of H₂ activation of **1** in comparison with the well-known B(C₆F₅)₃ was analyzed using DFT calculations in the gas phase and different solvents (CH₂Cl₂, *ortho*-difluorobenzene and acetonitrile). These investigations indicated that FLP chemistry based on **1** is considerably less favored than that with B(C₆F₅)₃. This is in agreement with control NMR experiments indicating hydride transfer from [H–B(Ohfp)₃][–] upon reaction with B(C₆F₅)₃, giving [H–B(C₆F₅)₃][–] and B(Ohfp)₃ in toluene and also MeCN. Induced by these unsuccessful reactions, the Lewis acidity towards HSAB hard and soft ions was investigated for gaining a deeper insight. A unified reference system based on the trimethylsilyl compounds Me₃Si–Y (Y = F, Cl, H, Me) and their respective ions Me₃Si⁺/Y[–] calculated at the G3 level was chosen as the anchor point. The individual ion affinities were then assessed based on subsequentisodesmic reactions calculated at a 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- ζ 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).

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Introduction

In the past few years, Lewis acids, especially their strongest representatives, have been of great interest and have found applications in catalysis, ionization, rearrangement reactions and bond heterolysis reactions.^{1–6} Naturally, tabulating the strengths of Lewis acids is very important and useful for esti-

imating 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 homogeneous medium on the basis of the well-known pH and pK_a scales that can be set as 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.^{7–9} 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 large 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.¹⁰ This concept was continued by many others.^{11–20} To avoid the problems that appear in the calculation of a “naked fluoride ion”, this approach was improved

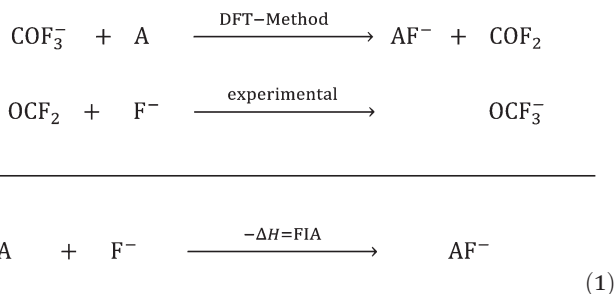
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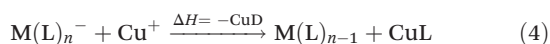
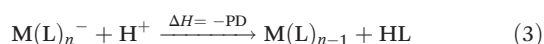
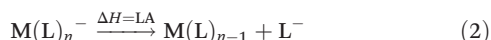


by using the experimental FIA of OCF_2 of 209 kJ mol^{-1} as an anchor point in a (pseudo-)isodesmic reaction (eqn (1)).²¹



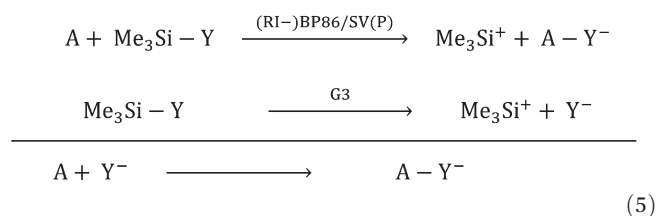
Using this method the strengths of many Lewis acids were classified.²² However, the fluoride ion is a hard base in the HSAB sense,²³ so the FIA may be deceptive for HSAB soft Lewis acids. Thus, it is advisable to compare methods with different approaches to find a convenient Lewis acid. Therefore, analogous to the FIA, the affinities to ions of varying hardness (*i.e.*, Cl^- , H^- and $\text{CH}_3^- = \text{Me}^-$) were used to rate the strengths of Lewis acids.^{17,24,25} 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, but also weakly coordinating anions (WCAs) have become an indispensable tool in chemistry and have found versatile applications. Boron^{26–29} or aluminum^{30,31} based WCAs were used for lithium ion batteries. Other WCAs stabilized reactive cations, *e.g.* $[\text{CX}_3]^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$),^{14,32,33} $[\text{P}_n\text{X}_m]^+$ ($\text{X} = \text{Br}, \text{I}$),³⁴ $[\text{N}_5]^+$,³⁵ $[\text{P}_9]^+$,³⁶ $[\text{AuXe}_4]^{2+}$,³⁷ $[\text{H}(\text{Et}_2\text{O})_2]^+$,³⁸ $[\text{Zn}_2]^{2+}$,³⁹ benzidine radical cations,⁴⁰ $[\text{Cu}(\text{S}_{12})(\text{S}_8)]^+$,⁴² $[\text{tBu}_3\text{Si-Ga-Si}(\text{tBu}_3)]^+$,⁴³ triarylsilylium or germylium ions,⁴⁴ protonated benzene,⁴⁵ and the 2-norbornyl cation.⁴⁶ Weakly bound complexes like those of ethene with copper,⁴⁸ silver⁴⁹ or gold are other examples.⁵⁰ Ion-like silylium ions coordinated to the carborates⁴¹ or the recent $\text{Me}_3\text{Si-F-Al}(\text{OC}(\text{CF}_3)_3)_3$ present strong Lewis acids.⁴⁷ Further WCA applications are catalytic C–F activation,⁵¹ ionic liquids^{52–58} and electrochemistry.^{59–67} 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.¹⁸ 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 (eqn (2)–(4)).



With the current contribution, we augmented the known scale¹⁸ 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 ($\text{X} = \text{F}, \text{C}, \text{H}, \text{Me}$), we chose a unified reference system. It is based on the trimethylsilyl compounds Me_3SiY ($\text{Y} = \text{F}, \text{Cl}, \text{H}, \text{Me}$) and their respective ions calculated at the G3 level as the anchor point. Thus, the relative values of the Lewis acidity towards different bases (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)), eqn (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- ζ basis.^{68–71} The error bar of this methodology was reported to be below 1 kJ mol^{-1} ,⁶⁹ and thus serves as a validation of the simpler isodesmic procedure according to eqn (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 $[\text{M}(\text{L})_n]^-$. All calculations were done in the gas phase.

Results and discussion

The background of these investigations has been experiments to activate hydrogen with the Lewis acid tris(2*H*-hexafluoroisopropoxy)borane ($\text{B}(\text{Ohfip})_3$ **1**), which has found applications in electrochemistry.⁷² We investigated the possibility of obtaining frustrated Lewis pair (FLP) chemistry⁷³ based on this Lewis acid and reacted it with H_2 and selected phosphanes, amines and *N*-heterocyclic carbenes (NHCs), but we have never observed a reaction. Even upon the 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^{57,74} as a rather stable WCA, and the FIA of the $\text{B}(\text{Ohfip})_3$ acid, calculated according to the procedure in eqn (5), is with 384 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 gaining a deeper insight. In the following we first describe our experiments before turning to the general calculations on a wide range of Lewis acids.



Synthesis and characterization

We synthesized **1** according to the literature and obtained white plate-like crystals melting at 32° C.⁷² 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.⁷⁵ The sum of the three O–B–O angles adds up to 360°, so apparently the orbital interactions of the π -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 $\text{Na}[\text{B}(\text{Ohfip})_4]$.⁵⁷ The C–O distances are with 141 pm nearly unchanged compared to those of HO-hfip.⁷⁶ 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 ($d_{\text{H}\cdots\text{O}} = 198$ pm). For each ligand, one CF_3 -group is above and the other is below this central plane. From a multitude of crystallization experiments with a large 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 °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, Fig. 1).

We were rather astonished to see this weak interaction, as the boron nitrogen distances in related complexes like $\text{MeCN}\cdot\text{BCl}_3$, $\text{MeCN}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ or the acetonitrile adduct of the perfluoroaryldiborane $\text{C}_6\text{F}_4\text{-1,2-B}(\text{C}_6\text{F}_5)_2$ are 156, 162 and 161 pm.^{77–79} The boron atoms of these complexes are distorted tetrahedrally coordinated. The hitherto longest boron nitrogen distance was measured in the mixed crystal $\text{MeCN}\cdot(\text{B}(\text{CH}_2\text{Ph})_3)_{0.92}(\text{Ga}(\text{CH}_2\text{Ph})_3)_{0.08}$ and amounts to 178 pm.⁸⁰ 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_3 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 with the well-known $\text{B}(\text{C}_6\text{F}_5)_3$ the standard Gibbs energies were calculated in the gas phase and different solvents (COSMO solvation model) by using a Born–Fajans–Haber cycle (Fig. 2, Table 1).

In agreement with our futile experimental efforts, Table 1 shows that FLP chemistry based on **1** is considerably less favored than that with $\text{B}(\text{C}_6\text{F}_5)_3$. 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 $\text{B}(\text{Ohfip})_3$ 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 $\text{B}(\text{Ohfip})_3$ and $\text{B}(\text{C}_6\text{F}_5)_3$, we did react $\text{K}^+[\text{HB}(\text{Ohfip})_3]^-$ with $\text{B}(\text{C}_6\text{F}_5)_3$ and expected to get neutral $\text{B}(\text{Ohfip})_3$ and $\text{K}^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$. This iso-desmic reaction was calculated by (RI-)BP86/SV(P) to be exothermic (-135 kJ mol⁻¹) and exergonic (-149 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 $\text{K}^+[\text{HB}(\text{Ohfip})_3]^-$ to a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene- d_8 immediately a white solid precipitated (mainly $\text{K}^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$). The broad singlet at 17.7 ppm in the ¹¹B NMR

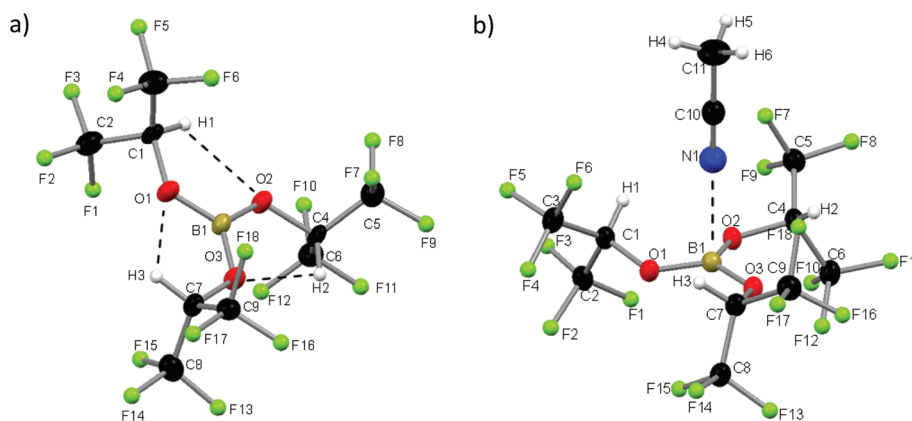


Fig. 1 Molecular structures of **1** and **1**·NCMe; thermal ellipsoids are shown at the 50% probability level. Fluorine atoms are drawn as spheres of arbitrary radius for clarity. Selected distances [pm] and angles [°]: (**1**): B1–O1 = 136.0(4), B1–O2 = 135.8(4), B1–O3 = 135.9(4), O1–C1 = 141.6(3), 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).



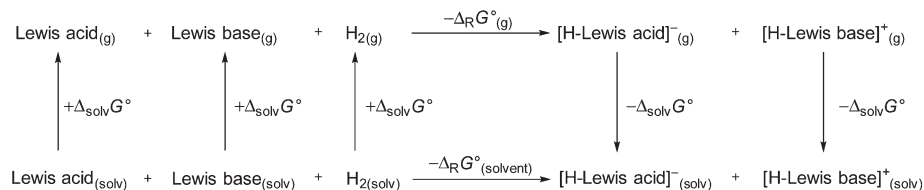


Fig. 2 Born-Haber-Fajans cycle to access the $\Delta_r G^\circ_{(g)}$ and $\Delta_r G^\circ_{(solvent)}$ of **1** and $B(C_6F_5)_3$ in various solvents.

Table 1 $\Delta_r G^\circ_{(g)}$ and $\Delta_r G^\circ_{(solvent)}$ 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

Vs. 1	$\Delta_r G^\circ_{(g)}$	$\Delta_r G^\circ(CH_2Cl_2)$	$\Delta_r G^\circ(o\text{-difluoro-benzene})$	$\Delta_r G^\circ(MeCN)$
Lewis base				
PMePh ₂	474	341	332	324
P ^t Bu ₃	464	191	174	155
NEt ₃	420	132	114	94
2,6-Lutidine	475	148	127	113
NHPh ₂	480	162	141	120
NHC	313	167	158	163
IDipp	310	53	37	3
Vs. $B(C_6F_5)_3$	$\Delta_r G^\circ_{(g)}$	$\Delta_r G^\circ(CH_2Cl_2)$	$\Delta_r G^\circ(o\text{-difluoro-benzene})$	$\Delta_r G^\circ(MeCN)$
Lewis base				
PMePh ₂	305	196	188	181
P ^t Bu ₃	292	54	39	22
NEt ₃	247	-5	-21	-39
2,6-Lutidine	308	25	6	-14
NHPh ₂	384	273	266	259
NHC	140	30	23	15
IDipp	137	-84	-98	-114

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 under an 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 ,⁸¹ (ii) in combination with $(C_6F_5)_2Ph_2P$ it leads to a FLP system capable of reversibly activating hydrogen⁸² and (iii) a mixture with P^tBu_3 is able to activate terminal alkynes.⁸³ 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 $NHPh_2$ or 2,6-lutidin, which are able to activate hydrogen in combination with $B(C_6F_5)_3$.⁸⁴ Since it appeared that the reactivity of **1** is not sufficient to activate H_2 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 ^{11}B NMR spectra at 0.8/1.3 ppm, but no detectable hydrogen activation occurred.

To investigate whether the Li^+ salt of the $[\text{HB}(\text{Ohfip})_3]^-$ anion and a protonated Lewis base like $[\text{HNEt}_3]^+\text{Cl}^-$ are compatible, we dissolved both salts in acetonitrile, and tested whether 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 of ion exchange (unlikely in polar MeCN) or that the small amounts of LiCl remain metastable as $[\text{LiCl}(\text{donor})_x]_y$ aggregates in solution. Overall, we have to note that H_2 activation might still be possible with this system, e.g. with bulkier NHCs as well as HD gas to look for scrambling and H_2 formation in the ^1H NMR spectrum, but at least not under our tested reaction conditions.

Quantum chemical investigations

Ion affinities of Lewis acids A. Earlier and the following calculations to determine ion affinities were based on isodesmic reactions (eqn (1) and (5)) with the BP86 functional^{85–87} and the SV(P) basis,⁸⁸ which represent good agreement between costs and accuracy. This method allows fast access to large molecules, which cannot be calculated at correlated levels. Basis reactions of the respective ion affinity calculations were the ion affinities of Me_3Si^+ against Y^- giving Me_3SiY ($\text{Y} = \text{F}, \text{Cl}, \text{H}, \text{Me}$), which were calculated at the reliable G3 level (Table 2).

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 BI_3 , AlCl_3 and AlI_3 .²² To validate and confirm the BP86/SV(P) values, we carried out RI-MP2 structure optimizations with TURBOMOLE^{89,90} and def2-QZVPP basis sets⁹¹ with the corresponding RI-C auxiliary bases for all atoms.⁹² Based on these structures, gas phase reaction energies were calculated according to eqn (6) with single point calculations at the CCSD(T)(FC)/double- ζ level plus an MP2 extrapolation of the correlation energy from double- ζ to quadruple- ζ basis sets with Gaussian 09 (ESI, S-Table 1†).⁹³

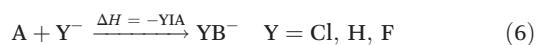


Table 2 Calculated reference reaction values (G3 level) as anchor points to determine FIA, CIA, HIA and MIA values

Reference systems	$\Delta_r H^\circ$ [kJ mol ⁻¹]
$\text{Me}_3\text{Si-F} \rightarrow \text{Me}_3\text{Si}^+ + \text{F}^-$	+958
$\text{Me}_3\text{Si-Cl} \rightarrow \text{Me}_3\text{Si}^+ + \text{Cl}^-$	+759
$\text{Me}_3\text{Si-H} \rightarrow \text{Me}_3\text{Si}^+ + \text{H}^-$	+959
$\text{Me}_3\text{Si-Me} \rightarrow \text{Me}_3\text{Si}^+ + \text{Me}^-$	+1000

Table 3 Overview of the CIA, HIA and FIA values [in kJ mol⁻¹] of chosen representative Lewis acids calculated via CCSD(T)(FC)/double- ζ level plus MP2 extrapolation to quadruple- ζ . The values in parentheses give the discrepancy to the affinity values calculated via eqn (5) at the BP86/SV(P) level

Lewis acid	CIA	HIA	FIA
BF_3	151 (5)	297 (-2)	346 (4)
BCl_3	195 (12)	395 (5)	384 (8)
BBr_3	219 (7)	440 (2)	425 (-16)
AlF_3	308 (1)	388 (-36)	482 (11)
AlCl_3	320 (3)	428 (-22)	502 (4)
AlBr_3	324 (-2)	425 (-39)	505 (-5)
GaF_3	319 (14)	444 (-18)	447 (13)
GaCl_3	299 (5)	446 (-19)	429 (-5)
GaBr_3	295 (1)	445 (-24)	426 (-13)
PF_5	165 (-14)	400 (-17)	380 (-17)
PCl_5	179 (2)	468 (-14)	393 (1)
AsF_5	237 (-14)	461 (-24)	434 (4)
SbF_5	333 (-8)	530 [517] ^b (-32/-13)	495 (2)
$\text{B}(\text{CN})_3$	363 (12)	583 (-3)	540 (-10)
$\text{B}(\text{OH})_3$	^a	163 (-7)	208 (4)

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

This approach was published earlier by Klopper *et al.*^{68,69} and has successfully been used by our group to study protonation equilibria.^{7–9}

The CIA and FIA values in Table 3 agree well with the values calculated by BP86/SV(P); however, some of the values may be off by up to 17 kJ mol⁻¹. The BP86/SV(P) HIA values of the boron halides, $\text{B}(\text{CN})_3$ and $\text{B}(\text{OH})_3$ nicely suit, since the B–H bond is less polar. Nevertheless, if the central atom is not a second row element, the bond becomes more polar or hydridic, so the HIA values may be approximately 20 kJ mol⁻¹ too 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 eqn (5) and with respect to the ion affinities of $\text{Me}_3\text{Si-Y}$ ($\text{Y} = \text{F}, \text{Cl}, \text{H}, \text{Me}$) at the G3 level (Table 5).

The HIA and MIA values of main group III halides (Table 4) follow similar trends and rise for the heavier halogen atoms. If we take a look at the affinity values of AlF_3 and GaF_3 there is not such a large difference compared to AlF_3 and BF_3 , since aluminum and gallium have nearly the same size and aluminum is just a little bit more electropositive than gallium. However, they differ in their affinity values towards soft or hard Lewis bases. AlF_3 favors the hard fluoride ion, while GaF_3



Table 4 Overview of 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(CF₃)₃)₃ can be attacked, depending on the nucleophile, at the Si or the Al atom and decomposes either to TMS-Y + F-Al(OC(CF₃)₃)₃ or TMS-F + Y-Al(OC(CF₃)₃)₃. The values for the nucleophilic attack at the Al atom are given in parentheses

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

^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 the start geometry. ⁹⁴ Unstable compounds and the values of unstable compounds are given in italics.

prefers softer Lewis bases like Me⁻ or H⁻ anions, which confirms that aluminum trifluoride is harder than gallium trifluoride. Nevertheless, if the halide ligands become heavier, gallium turns out scaled by aluminum, which indicates that the GaX₃ Lewis acids are more stable and less acidic. This could mean that the overlap of the π orbitals is more pronounced and hence the π back bonding is stronger. To summarize, in this row, the AlX₃ compounds are the strongest Lewis acids with respect to fluoride and chloride, but towards the hydride ion, GaX₃ acids are stronger and with respect to the methanide ion similar to the aluminum acids. The CIA and FIA values of PF₅ and PCl₅ 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 SbF₅, 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.

Putting boron acids in context. As expected, B(OH)₃ is a quite weak Lewis acid and since $[\text{B}(\text{OH})_3\text{Cl}]^-$ is experimentally unknown, we disregarded this anion from our calculations. Compound **1** reveals relatively low ion affinity values. Compared to B(C₆F₅)₃ the FIA value of **1** is just 68 kJ mol⁻¹ lower, but the HIA value is 136 kJ mol⁻¹ lower. This huge difference in the HIA value may explain our experimentally observed results. Similarly, the HIA of B(C₆F₅)₃ is nearly identical with that one of the *versus* fluoride considerably stronger Lewis acid Al(C₆F₅)₃. B(C₁₂F₉)₃ and B(C₆H₃(CF₃)₂)₃ show the same effect, which implies that boron Lewis acids stabilize the hydride ion better than other Lewis acids A with more electropositive central atoms like Al. These results are in agreement with

HSAB-arguments: **1** and Al(C₆F₅)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(C₁₂F₉)₃ result from the sterically demanding perfluorinated biphenyl ligands, which hinder the access to the Lewis acid center. Since F₄C₆(1,2-(B(C₆F₅)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 non-bridged geometry is smaller than 1 kJ mol⁻¹.

Group 14 acids. Main group IV is represented by the silylium zwitterion SiMe₂CH₂CB₁₁Cl₁₁,⁹⁵ and the Janus-headed Lewis acid TMS-F-Al(OC(CF₃)₃)₃.⁴⁷ The ion affinity of the silylium zwitterion is boosted by around 140 kJ mol⁻¹ compared to the silicon atom in neutral TMS-F-Al(OC(CF₃)₃)₃, which itself features IAs only slightly inferior to B(C₆F₅)₃.

Lewis superacids. Since SbF₅ is viewed as the strongest conventional Lewis acid, the FIA value of monomeric SbF₅ is used to determine Lewis superacids: "Molecular Lewis acids, which are stronger than monomeric SbF₅ in the gas phase are Lewis superacids."⁹⁶ 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 AlCl₃, AlBr₃, AlI₃, Al(OC(CF₃)₃)₃, B(OTeF₅)₅, As(OTeF₅)₅, Sb(OTeF₅)₅, B(CN)₃, B(CF₃)₃, Al(C₆F₅)₃, F₄C₆(1,2-(B(C₆F₅)₂)₂) and SiMe₂CH₂CB₁₁Cl₁₁ excel the FIA value of SbF₅ and may be classified as Lewis superacids. However, P-based acids like PF₂(C₂F₅)₃ possess, compared to PF₅, 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 the LUMO level. To gain a deeper insight into the relationship between the ion affinity values and the LUMO levels of the Lewis acids in Table 4, we plotted the values and added a regression line in each case (see Fig. 3).

By trend, the gradient shows that a low LUMO level is accompanied by 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 interactions 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 obtains a more covalent character and fits the trend slightly better than chloride.

Stability of WCAs based on FIA, PD, CuD, and HOMO levels and the HOMO–LUMO gap. If the above mentioned Lewis acids are expanded by an 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 4. 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 (eqn (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 using the Sackur–Tetrode equation.^{97–99} 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.¹⁸ The lower the HOMO energy, the more resistant is an anion towards oxidation and hence the electron is harder to remove. The HOMO–LUMO gap is related to its resistance towards reduction. The larger the gap, the more

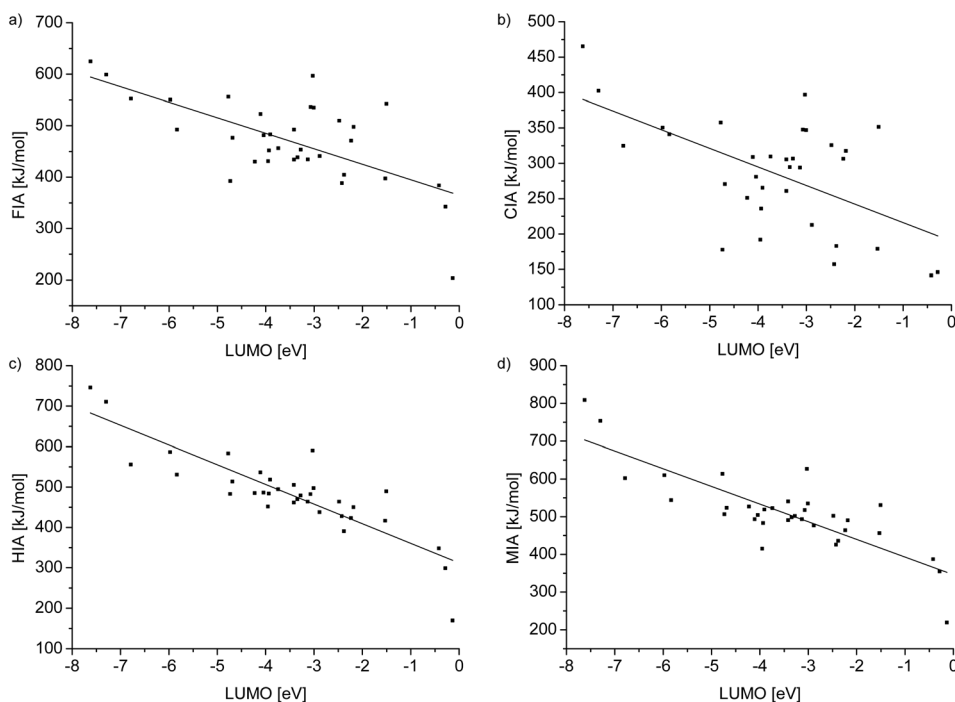


Fig. 3 Plots showing the regression lines of the relationships between the ion affinity values and the LUMO level of the Lewis acids collected in Table 4. Linear regression of ion affinity values against the LUMO level for (a): $y = -30.14(6.05)x + 364.61(24.86)$, $R^2 = 0.41$, (b): $y = -26.31(6.71)x + 189.68(26.85)$, $R^2 = 0.31$, (c): $y = -48.68(5.06)x + 311.86(19.98)$, $R^2 = 0.73$ and (d): $y = -46.90(5.75)x + 345.77(22.68)$, $R^2 = 0.67$.



Table 5 Calculated properties of WCAs: FIA of the parent Lewis acid as shown in Table 4

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

stable is the WCA towards gaining an electron. The data in Table 5 cannot be taken as absolute, but since the same calculation methods were used, relative trends will definitely be correct.

Among the [MX₄]⁻ anions (M = B, Al, Ga; X = F, Cl, Br, I) the [MF₄]⁻ and [MCl₄]⁻ anions are exceptionally stable towards reduction (see gap), and the [MF₄]⁻ and [MI₄]⁻ 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 alkoxy-aluminate [Al(OC(CF₃)₃)₄]⁻ 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 levels), but it is significantly more reduction resistant. These values underline its current role in chemistry to stabilize highly reactive cations.^{14,33,38,39,42,43,48–50,100,101} In addition, Table 5 includes a series of WCAs with (mainly fluorinated) organic ligands. Of those, [B(CN)₄]⁻ and [B(CF₃)₄]⁻ offer very good WCA properties, although [B(CF₃)₄]⁻ allows for additional decomposition pathways.¹⁰² Typically, the fluorination of ligands increases the stability values of borate based anions.¹⁸ Apart from that, the

stability values of all the WCAs including M–C bonds are quite similar.

Conclusions

Attempts to use the conveniently available B(Ohfp)₃ as a Lewis acid component in FLP chemistry systems failed in our hands for a wide range of neutral Lewis bases and with all the used reaction conditions. However, it may well be possible using the right bases (*e.g.* bulky NHCs), solvents other 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 (Me₃Si–Y/Me₃Si⁺/Y⁻; Y = Cl, H, F, Me). Validation was performed at the highly reliable ccsd(t)/DZ→QZ level for a subset of 15 smaller Lewis acids MX_n. These values with an error bar below 1 kJ mol⁻¹ are currently the best available benchmark calculations on Lewis acidity for these systems. With the consistent reference system and a set ofisodesmic reactions, we calculated the CIA, HIA, FIA and MIA values of 33 common and frequently used, partly rather large Lewis acids (Table 4). With this approach, comparable ion affinity values were obtained for four different Lewis bases 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 (H_2O and O_2 <1 ppm). Special J. Young NMR tubes sealed with Teflon valves were used to exclude air and moisture. All solvents were dried over CaH_2 or P_4O_{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⁺ 400 MHz WB spectrometer. ^1H and ^{13}C chemical shifts are given with respect to TMS, ^{19}F NMR spectra to fluorotrichloromethane, ^{11}B NMR spectra to the boron-trifluoride-diethyl-ether-complex, ^{31}P NMR spectra to a 85% phosphoric(v) acid solution and ^7Li NMR spectra to 9.7 M LiCl in D_2O . 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 $\text{MoK}\alpha$ radiation. The single crystals were mounted in perfluoroether oil on a MiTeGen MicromountTM. $\text{B}(\text{Ohfp})_3$ has CCSD deposition number 1004582 and the MeCN-adduct 1004583.

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References

- S. J. Geier, P. A. Chase and D. W. Stephan, *Chem. Commun.*, 2010, **46**, 4884–4886.
- T. Krahl and E. Kemnitz, *J. Fluorine Chem.*, 2006, **127**, 663–678.
- S. N. Kessler and H. A. Wegner, *Org. Lett.*, 2010, **12**, 4062–4065.
- M. Tobisu and N. Chatani, *Angew. Chem., Int. Ed.*, 2006, **45**, 1683–1684.
- A. W. Schmidt and H. J. Knolker, *Synlett*, 2010, 2207–2239.
- D. W. Stephan, *Org. Biomol. Chem.*, 2008, **6**, 1535–1539.
- D. Himmel, S. K. Goll, I. Leito and I. Krossing, *Angew. Chem., Int. Ed.*, 2010, **49**, 6885–6888.
- D. Himmel, S. K. Goll, I. Leito and I. Krossing, *Chem. – Eur. J.*, 2011, **17**, 5808–5826.
- D. Himmel, S. K. Goll, I. Leito and I. Krossing, *Chem. – Eur. J.*, 2012, **18**, 9333–9340.
- T. E. Mallouk, G. L. Rosenthal, G. Muller, R. Brusasco and N. Bartlett, *Inorg. Chem.*, 1984, **23**, 3167–3173.
- H. D. B. Jenkins, H. K. Roobottom and J. Passmore, *Inorg. Chem.*, 2003, **42**, 2886–2893.
- K. O. Christe and H. D. B. Jenkins, *J. Am. Chem. Soc.*, 2003, **125**, 9457–9461.
- T. S. Cameron, R. J. Deeth, I. Dionne, H. B. Du, H. D. B. Jenkins, I. Krossing, J. Passmore and H. K. Roobottom, *Inorg. Chem.*, 2000, **39**, 5614–5631.
- I. Krossing, A. Bihlmeier, I. Raabe and N. Trapp, *Angew. Chem., Int. Ed.*, 2003, **42**, 1531–1534.
- H. D. B. Jenkins, I. Krossing, J. Passmore and I. Raabe, *J. Fluorine Chem.*, 2004, **125**, 1585–1592.
- L. A. Muck, A. Y. Timoshkin and G. Frenking, *Inorg. Chem.*, 2012, **51**, 640–646.
- A. Y. Timoshkin and G. Frenking, *Organometallics*, 2008, **27**, 371–380.
- I. Krossing and I. Raabe, *Chem. – Eur. J.*, 2004, **10**, 5017–5030.
- A. Kraft, J. Beck and I. Krossing, *Chem. – Eur. J.*, 2011, **17**, 12975–12980.
- A. Kraft, N. Trapp, D. Himmel, H. Bohrer, P. Schluter, H. Scherer and I. Krossing, *Chem. – Eur. J.*, 2011, **18**, 9371–9380.
- K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson, J. A. Sheehy and J. A. Boatz, *J. Fluorine Chem.*, 2000, **101**, 151–153.
- L. O. Muller, D. Himmel, J. Stauffer, G. Steinfeld, J. Slattery, G. Santiso-Quinones, V. Brecht and I. Krossing, *Angew. Chem., Int. Ed.*, 2008, **47**, 7659–7663.
- R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533–3539.
- M. T. Mock, R. G. Potter, D. M. Camaioni, J. Li, W. G. Dougherty, W. S. Kassel, B. Twamley and D. L. DuBois, *J. Am. Chem. Soc.*, 2009, **131**, 14454–14465.
- E. R. Clark, A. Del Grosso and M. J. Ingleson, *Chem. – Eur. J.*, 2013, **19**, 2462–2466.
- J. Barthel, M. Wuhr, R. Buestrich and H. J. Gores, *J. Electrochem. Soc.*, 1995, **142**, 2527–2531.
- J. Barthel, R. Buestrich, H. J. Gores, M. Schmidt and M. Wuhr, *J. Electrochem. Soc.*, 1997, **144**, 3866–3870.
- J. Barthel, R. Buestrich, E. Carl and H. J. Gores, *J. Electrochem. Soc.*, 1996, **143**, 3565–3571.
- J. Barthel, R. Buestrich, E. Carl and H. J. Gores, *J. Electrochem. Soc.*, 1996, **143**, 3572–3575.
- S. M. Ivanova, B. G. Nolan, Y. Kobayashi, S. M. Miller, O. P. Anderson and S. H. Strauss, *Chem. – Eur. J.*, 2001, **7**, 503–510.



- 31 S. Tsujioka, B. G. Nolan, H. Takase, B. P. Fauber and S. H. Strauss, *J. Electrochem. Soc.*, 2004, **151**, A1418–A1423.
- 32 H. P. A. Mercier, M. D. Moran, G. J. Schrobilgen, C. Steinberg and R. J. Suontamo, *J. Am. Chem. Soc.*, 2004, **126**, 5533–5548.
- 33 A. J. Lehner, N. Trapp, H. Scherer and I. Krossing, *Dalton Trans.*, 2010, **40**, 1448–1452.
- 34 M. Gonsior, I. Krossing, L. Muller, I. Raabe, M. Jansen and L. van Wullen, *Chem. – Eur. J.*, 2002, **8**, 4475–4492.
- 35 K. O. Christe, W. W. Wilson, J. A. Sheehy and J. A. Boatz, *Angew. Chem., Int. Ed.*, 2001, **40**, 2947–2947.
- 36 T. Kochner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani and I. Krossing, *Angew. Chem., Int. Ed.*, 2012, **51**, 6529–6531.
- 37 S. Seidel and K. Seppelt, *Science*, 2000, **290**, 117–118.
- 38 I. Krossing and A. Reisinger, *Eur. J. Inorg. Chem.*, 2005, 1979–1989.
- 39 S. Schulz, D. Schuchmann, I. Krossing, D. Himmel, D. Blaser and R. Boese, *Angew. Chem., Int. Ed.*, 2009, **48**, 5748–5751.
- 40 X. Y. Chen, B. B. Ma, X. Y. Wang, S. X. Yao, L. C. Ni, Z. Y. Zhou, Y. Z. Li, W. Huang, J. Ma, J. L. Zuo and X. P. Wang, *Chem. – Eur. J.*, 2012, **18**, 11828–11836.
- 41 C. A. Reed, *Acc. Chem. Res.*, 2010, **43**, 121–128.
- 42 G. Santiso-Quinones, R. Brückner, C. Knapp, I. Dionne, J. Passmore and I. Krossing, *Angew. Chem., Int. Ed.*, 2009, **48**, 1133–1137.
- 43 A. Budanow, T. Sinke, J. Tillmann, M. Bolte, M. Wagner and H. W. Lerner, *Organometallics*, 2012, **31**, 7298–7301.
- 44 A. Schäfer, M. Reißmann, S. Jung, A. Schäfer, W. Saak, E. Brendler and T. Müller, *Organometallics*, 2013, **32**, 4713–4722.
- 45 F. Scholz, D. Himmel, L. Eisele, W. Unkrig and I. Krossing, *Angew. Chem., Int. Ed.*, 2014, **53**, 1689–1692.
- 46 F. Scholz, D. Himmel, F. W. Heinemann, P. V. Schleyer, K. Meyer and I. Krossing, *Science*, 2013, **341**, 62–64.
- 47 M. Rohde, L. O. Müller, D. Himmel, H. Scherer and I. Krossing, *Chem. – Eur. J.*, 2014, **20**, 1218–1222.
- 48 G. Santiso-Quinones, A. Reisinger, J. Slattery and I. Krossing, *Chem. Commun.*, 2007, 5046–5048.
- 49 I. Krossing and A. Reisinger, *Angew. Chem., Int. Ed.*, 2003, **42**, 5725–5728.
- 50 J. Schaefer, D. Himmel and I. Krossing, *Eur. J. Inorg. Chem.*, 2013, 2712–2717.
- 51 G. Meier and T. Braun, *Angew. Chem., Int. Ed.*, 2009, **48**, 1546–1548.
- 52 P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772–3789.
- 53 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.
- 54 A. Bosmann, G. Francio, E. Janssen, M. Solinas, W. Leitner and P. Wasserscheid, *Angew. Chem., Int. Ed.*, 2001, **40**, 2697–2699.
- 55 T. Timofte, S. Pitula and A. V. Mudring, *Inorg. Chem.*, 2007, **46**, 10938–10940.
- 56 I. Raabe, K. Wagner, K. Guttsche, M. K. Wang, M. Gratzel, G. Santiso-Quinones and I. Krossing, *Chem. – Eur. J.*, 2009, **15**, 1966–1976.
- 57 S. Bulut, P. Klose and I. Krossing, *Dalton Trans.*, 2011, **40**, 8114–8124.
- 58 F. Scholz, D. Himmel, H. Scherer and I. Krossing, *Chem. – Eur. J.*, 2013, **19**, 109–116.
- 59 M. G. Hill, W. M. Lamanna and K. R. Mann, *Inorg. Chem.*, 1991, **30**, 4687–4690.
- 60 P. G. Gassman and P. A. Deck, *Organometallics*, 1994, **13**, 1934–1939.
- 61 P. G. Gassman, J. R. Sowa, M. G. Hill and K. R. Mann, *Organometallics*, 1995, **14**, 4879–4885.
- 62 L. Pospisil, B. T. King and J. Michl, *Electrochim. Acta*, 1998, **44**, 103–108.
- 63 R. J. LeSuer and W. E. Geiger, *Angew. Chem., Int. Ed.*, 2000, **39**, 248–250.
- 64 N. Camire, U. T. Mueller-Westerhoff and W. E. Geiger, *J. Organomet. Chem.*, 2001, **637**, 823–826.
- 65 F. Barriere, N. Camire, W. E. Geiger, U. T. Mueller-Westerhoff and R. Sanders, *J. Am. Chem. Soc.*, 2002, **124**, 7262–7263.
- 66 N. Camire, A. Nafady and W. E. Geiger, *J. Am. Chem. Soc.*, 2002, **124**, 7260–7261.
- 67 W. E. Geiger and F. Barriere, *Acc. Chem. Res.*, 2010, **43**, 1030–1039.
- 68 W. Klopffer and H. P. Luthi, *Mol. Phys.*, 1999, **96**, 559–570.
- 69 A. D. Boese, J. M. L. Martin and W. Klopffer, *J. Phys. Chem. A*, 2007, **111**, 11122–11133.
- 70 P. Jurecka and P. Hobza, *Chem. Phys. Lett.*, 2002, **365**, 89–94.
- 71 P. Jurecka and P. Hobza, *J. Am. Chem. Soc.*, 2003, **125**, 15608–15613.
- 72 H. S. Lee, X. Q. Yang, C. L. Xiang, J. McBreen and L. S. Choi, *J. Electrochem. Soc.*, 1998, **145**, 2813–2818.
- 73 D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46–76.
- 74 L. Alvarez, *Li[B(OC(H)(CF₃)₂)₄] – Synthesis, Optimization and Characterization of its Electrolytes*, University of Freiburg, Freiburg, 2013.
- 75 M. Kuprat, R. Kuzora, M. Lehmann, A. Schulz, A. Villinger and R. Wustrack, *J. Organomet. Chem.*, 2010, **695**, 1006–1011.
- 76 A. Berkessel, J. A. Adrio, D. Huettenhain and J. M. Neudorfl, *J. Am. Chem. Soc.*, 2006, **128**, 8421–8426.
- 77 B. Swanson, D. F. Shriver and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 2182–2189.
- 78 H. Jacobsen, H. Berke, S. Doring, G. Kehr, G. Erker, R. Frohlich and O. Meyer, *Organometallics*, 1999, **18**, 1724–1735.
- 79 P. A. Chase, L. D. Henderson, W. E. Piers, M. Parvez, W. Clegg and M. R. J. Elsegood, *Organometallics*, 2006, **25**, 349–357.
- 80 B. Neumuller and F. Gahlmann, *Z. Anorg. Allg. Chem.*, 1992, **612**, 123–129.



- 81 G. C. Welch, T. Holtrichter-Roessmann and D. W. Stephan, *Inorg. Chem.*, 2008, **47**, 1904–1906.
- 82 L. Greb, P. Ona-Burgos, B. Schirmer, S. Grimme, D. W. Stephan and J. Paradies, *Angew. Chem., Int. Ed.*, 2012, **51**, 10164–10168.
- 83 M. A. Dureen and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 8396–8397.
- 84 S. J. Geier and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 3476–3477.
- 85 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.
- 86 J. P. Perdew, *Phys. Rev. B: Condens. Matter*, 1986, **33**, 8822–8824.
- 87 J. P. Perdew, *Phys. Rev. B: Condens. Matter*, 1986, **34**, 7406–7406.
- 88 A. Schafer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571–2577.
- 89 R. Ahlrichs, M. Bar, M. Haser, H. Horn and C. Kolmel, *Chem. Phys. Lett.*, 1989, **162**, 165–169.
- 90 O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, 1995, **102**, 346–354.
- 91 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
- 92 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.
- 93 G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford, CT, 2004.
- 94 G. Laus, A. Schwarzler, P. Schuster, G. Bentivoglio, M. Hummel, K. Wurst, V. Kahlenberg, T. Lorting, J. Schutz, P. Peringer, G. Bonn, G. Nauer and H. Schottenberger, *Z. Naturforsch., B: Chem. Sci.*, 2007, **62**, 295–308.
- 95 R. Ramirez-Contreras, N. Bhuvanesh, J. Zhou and O. V. Ozerov, *Angew. Chem., Int. Ed.*, 2013, **52**, 10313–10315.
- 96 L. O. Müller, D. Himmel, J. Stauffer, G. Steinfeld, J. Slattery, G. Santiso-Quinones, V. Brecht and I. Krossing, *Angew. Chem., Int. Ed.*, 2008, **47**, 7659–7663.
- 97 H. Tetrode, *Ann. Phys.*, 1912, **38**, 434–442.
- 98 O. Sackur, *Ann. Phys.*, 1911, **36**, 958–980.
- 99 O. Sackur, *Ann. Phys.*, 1913, **40**, 67–86.
- 100 T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani and I. Krossing, *Angew. Chem., Int. Ed.*, 2012, **51**, 6529–6531.
- 101 I. Raabe, D. Himmel, S. Mueller, N. Trapp, M. Kaupp and I. Krossing, *Dalton Trans.*, 2008, 946–956.
- 102 M. Finze, E. Bernhardt, M. Zahres and H. Willner, *Inorg. Chem.*, 2004, **43**, 490–505.

