From unsuccessful H₂-activation with FLPs containing B(Ohfip)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(Ohfip)₃, 1 (Ohfip = 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(Ohfip)₂]⁻ upon reaction with B(C₆F₅)₃, giving [H–B(C₆F₅)₃]⁻ and B(Ohfip) 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 subsequent isodesmic 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).

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 estimating 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 pKₐ 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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† Electronic supplementary information (ESI) available: Experimental procedures and spectroscopic data are included in the supporting information, as well as detailed energies, vibrational frequencies, xyz-coordinates, solvation energy calculations, HOMO-LUMO-gaps and other data on the computations (>700 pages). CCDC 1004582 and 1004583. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt02822h.
‡ Dr Nils Trapp is now working with ETH Zürich.
by using the experimental FIA of OCF₂ of 209 kJ mol⁻¹ as an anchor point in a (pseudo-)isodesmic reaction (eqn (1)).

\[
\begin{align*}
\text{COF}_3^- + A & \xrightarrow{\text{DFT-Metho}} \text{AF}^- + \text{COF}_2 \\
\text{OCF}_2^- + F^- & \xrightarrow{\text{experimental}} \text{OCF}_3^-
\end{align*}
\]

Using this method the strengths of many Lewis acids were classified. However, the fluoride ion is a hard base in the HSAB sense, 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 CH₃⁻) were used to rate the strengths of Lewis acids. 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 or aluminum based WCAs were used for lithium ion batteries. Other WCAs stabilized reactive cations, e.g., [CX₃]⁺ (X = Cl, Br, I), [P₉Xm⁻] (X = Br, I), [N₅]⁺, [P₉]⁺, [AuXe₄]²⁺, [H(Et₂O)₂]⁺, [Zn₂]²⁺, [H(B(OH)(CF₃)₃)]⁻, [B(Ohfip)₃]⁻ triarylsilylum or germilyum ions, protonated benzene, and the 2-norbornyl cation. Weakly bound complexes like those of ethene with copper, silver or gold are other examples. Ion-like silylium ions coordinated to the carbanions [Cu(S₁₂)(S₈)]⁺, [P₉]⁺, [AuXe₄]²⁺, [H(B(OH)(CF₃)₃)]⁻, [B(Ohfip)₃]⁻ are comparable based on unified reference systems. It is a rather stable WCA, and the FIA of the fluoride ion a-totally occurring in equilibrium. By contrast, the respective anion [B(Ohfip)]⁻ is known as a rather stable WCA, and the FIA of the B(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 [B(Ohfip)]⁻ from Na[B(H₃)₄] and HO-hfip, the [H–B(Ohfip)]⁻ 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 [H–B(Ohfip)]⁻ 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.² The Lewis acid 1 crystallizes in the monoclinic space group P2₁/c and exists, in contrast to the dimeric heavier homologue Al(Ohfip)₃, as a monomer.⁷ 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 Na[B(Ohfip)₄].⁵⁷ The C–O distances are with 141 pm nearly unchanged compared to those of HO-hfip.⁷⁶ Interestingly, the central B(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_HO = 198 pm). For each ligand, one CF₃-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 MeCN·B(C₆F₅)₃, MeCN·B(C₆F₅)₃ or the acetonitrile adduct of the perfluoroaryl diborane C₆F₅·B(C₆F₅)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 MeCN·B(C₆F₅)₃·CH₃CN·BCl₃, MeCN·B(C₆F₅)₃ or the acetonitrile adduct of the acetonitrile molecule (248 pm, Fig. 1). 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).

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 B(C₆F₅)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 B(C₆F₅)₃. Furthermore, these investigations suggested that polar solvents promote H₂ 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 CH₂Cl₂ and did not observe any desired chemistry with H₂ but noted that the liquid B(Ohfip)₃ forms two immiscible phases in CH₂Cl₂. 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(C₆F₅)₃, we did react K+[HB(Ohfip)₃] + with B(C₆F₅)₃ and expected to get neutral B(Ohfip)₃ and K+[HB(C₆F₅)₃]. This isodesmic reaction was calculated by (RI–JP86/SVP) 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 K+[HB(Ohfip)₃]⁻ to a solution of B(C₆F₅)₃ in toluene-d₈ immediately a white solid precipitated (mainly K+[HB(C₆F₅)₃]⁻). The broad singlet at 17.7 ppm in the¹¹B 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 $\Delta_r G^{(g)}$ and $\Delta_r G^{(solvent)}$ of 1 and B(C$_6$F$_5$)$_3$ in various solvents.

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

<table>
<thead>
<tr>
<th>Vs. 1</th>
<th>$\Delta_r G^{(g)}$</th>
<th>$\Delta_r G^{(CH_2Cl_2)}$</th>
<th>$\Delta_r G^{(o-difluoro-benzene)}$</th>
<th>$\Delta_r G^{(MeCN)}$</th>
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<td>Lewis base</td>
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</tr>
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<td>PMePh$_2$</td>
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<td>324</td>
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<td>P'Bu$_3$</td>
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<td>155</td>
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<td>113</td>
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<tr>
<td>IDipp</td>
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<td>37</td>
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<tr>
<td>B(C$_6$F$_5$)$_3$</td>
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<tr>
<td>Lewis base</td>
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<td>$\Delta_r G^{(CH_2Cl_2)}$</td>
<td>$\Delta_r G^{(o-difluoro-benzene)}$</td>
<td>$\Delta_r G^{(MeCN)}$</td>
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<td>196</td>
<td>188</td>
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<td>P'Bu$_3$</td>
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<tr>
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<tr>
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<td>6</td>
<td>-14</td>
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<tr>
<td>NHPh$_2$</td>
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<td>266</td>
<td>259</td>
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<tr>
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<td>30</td>
<td>23</td>
<td>15</td>
</tr>
<tr>
<td>IDipp</td>
<td>137</td>
<td>-84</td>
<td>-98</td>
<td>-114</td>
</tr>
</tbody>
</table>

spectra of the solution revealed that B(Ohfip)$_3$ had formed, but only a very weak signal of scarcely soluble K$^+$$[\text{HB(C}_6\text{F}_5\text{)}_3]^{-}$ (at around −25 ppm, $J_{\text{H},\text{B}} \approx 84$ Hz) and no remaining B(C$_6$F$_5$)$_3$ or [HB(Ohfip)$_3$]$^{-}$ was observed. After removing most of the solution with a syringe, deuterated MeCN was added to examine the now soluble precipitate. The $^{11}$B NMR spectrum shows mainly the doublet of $[\text{HB(C}_6\text{F}_5\text{)}_3]^{-}$ at the typical values $\delta^{11}\text{B} = -25.4$ ($J_{\text{H},\text{B}}$ = 93 Hz). Since it was not possible to get rid of all the solution, still a small signal of scarcely soluble K$^+$$[\text{HB(C}_6\text{F}_5\text{)}_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$_6$F$_5$)$_3$]$^{-}$ 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$_6$F$_5$)$_3$]$^{-}$. This seems reasonable, since B(C$_6$F$_5$)$_3$ 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$_6$F$_5$)$_3$ (i) forms an adduct with PPh$_3$, (ii) in combination with (C$_6$F$_5$)Ph$_2$P and (iii) a mixture with P'Bu$_3$ is able to activate terminal alkynes. Here PPh$_3$, P'Bu$_3$ and P'MePh$_2$ did not form classical adducts with 1, and there is no sign of a hydrogen activation (e.g. doublet $J_{\text{P},\text{H}}$ in the $^{31}$P NMR, doublet $J_{\text{B},\text{H}}$ 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-lutidine, which are able to activate hydrogen in combination with B(C$_6$F$_5$)$_3$.$^{84}$ 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 [HB(Ohfip)$_3$]$^{-}$ anion and a protonated Lewis base like [HN$\text{Et}_{3}$]$^{+}$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 [LiCl(donor)]$_3^-$ 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 $^{2}$H 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$_3$Si$^+$ against Y$^-$ giving Me$_3$SiY (Y = F, Cl, H, 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$_3$. To validate and confirm the BP86/SV(P) values, we carried out RI-MP2 structure optimizations with TURBOMOLE$^{89,90}$ and def2-QZVPB basis sets$^{91}$ with the corresponding RI-C auxiliary bases for all atoms. Based on these structures, gas phase reaction energies were calculated according to eqn (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).$^{93}$

\[
A + Y^- \rightarrow \Delta H_{f} = \Delta H_{f}^{\text{YIA}} \ YB^- \quad Y = \text{Cl, H, F}
\] (6)

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

<table>
<thead>
<tr>
<th>Reference systems</th>
<th>$\Delta H_{f}^{\text{YIA}}$ [kJ mol$^{-1}$]</th>
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<tbody>
<tr>
<td>Me$_3$Si-F $\rightarrow$ Me$_3$Si$^+$ + F$^-$</td>
<td>958</td>
</tr>
<tr>
<td>Me$_3$Si-Cl $\rightarrow$ Me$_3$Si$^+$ + Cl$^-$</td>
<td>759</td>
</tr>
<tr>
<td>Me$_3$Si-H $\rightarrow$ Me$_3$Si$^+$ + H$^+$</td>
<td>959</td>
</tr>
<tr>
<td>Me$_3$Si-Me $\rightarrow$ Me$_3$Si$^+$ + Me$^+$</td>
<td>1000</td>
</tr>
</tbody>
</table>

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-$\zeta$ level plus MP2 extrapolation to quadruple-$\zeta$. The values in parentheses give the discrepancy to the affinity values calculated via eqn (5) at the BP86/SV(P) level

<table>
<thead>
<tr>
<th>Lewis acid</th>
<th>CIA</th>
<th>HIA</th>
<th>FIA</th>
</tr>
</thead>
</table>

$^a$ Does not form a complex. $^b$[SbF$_5$H]$^-$ is not stable and would decompose to SbF$_4^-$ + 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, B(CN)$_3$ and 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 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 Me$_3$Si–Y (Y = F, Cl, H, 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

<table>
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<tr>
<th>Lewis acid</th>
<th>LUMO [eV]</th>
<th>CIA [kJ mol⁻¹]</th>
<th>HIA [kJ mol⁻¹]</th>
<th>FIA [kJ mol⁻¹]</th>
<th>MIA [kJ mol⁻¹]</th>
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<th>LUMO [eV]</th>
<th>CIA [kJ mol⁻¹]</th>
<th>HIA [kJ mol⁻¹]</th>
<th>FIA [kJ mol⁻¹]</th>
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The anion containing a B–Y–B bridge is thermodynamically favored. The most stable isomer was used. The experimental crystal structure was used as the start geometry. Unstable compounds and the values of unstable compounds are given in italics.
demand of the C\textsubscript{2}F\textsubscript{5} groups in the acid–base complexes. The HIA of PF\textsubscript{2}(C\textsubscript{2}F\textsubscript{5})\textsubscript{3} is a bit higher, since H\textsuperscript{−} is small and the steric effect of the C\textsubscript{2}F\textsubscript{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\textsuperscript{−} 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\textsuperscript{+}) and a soft electrophile (Cu\textsuperscript{+}) 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 \( \Delta U \) values, the \( \Delta G^\circ \) values of the PD and CuD; hence they are closer to laboratory conditions.

The entropy \( S \) of the H\textsuperscript{+} and Cu\textsuperscript{+} cations was calculated using the Sackur–Tetrode equation. 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. 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

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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): \( y = -90.14(6.05)x + 364.61(24.86) \), \( R^2 = 0.41 \), (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): \( y = -46.90(5.75)x + 345.77(22.68) \), \( R^2 = 0.67 \).
Although \([\text{B(CF}_3\text{)}_4]\) can be considered a ligand at the central atom to enhance the nucleophile (see PD and CuD). This confirms that especially increased resistance against an attack of a soft or a hard base is expected for these systems. With the consistent reference system currently the best available benchmark calculations on Lewis acids MX₄. These values with an error bar below 1 kJ mol⁻¹ represent the current role in chemistry to stabilize highly reactive Lewis acid MX₄. These values with an error bar below 1 kJ mol⁻¹ can 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 [MCl₄]⁻ anions have an increased resistance against an attack of a soft or a hard base. 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 alkoxyluminate [Al(OC(F₆)₃)₃]⁻ 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.14,15,16,39,42,41,48,50,50,100,101

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. Typically, the fluorination of ligands increases the stability values of borate based anions. 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(Ohfip), 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⁻→QZ level for a subset of 15 smaller Lewis acids MX₄⁻. 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 of isodesmic 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 (H₂O and O₂ < 1 ppm). Special J. Young NMR tubes sealed with Teflon valves were used to exclude air and moisture. All solvents were dried over CaH₂ or P₂O₅ and distilled afterwards. NMR data were recorded from solutions in d₈-toluene or d₃-acetonitrile at room temperature on a Bruker AVANCE II 400 MHz WB spectrometer. ¹H and ¹³C chemical shifts are given with respect to TMS, ¹⁹F NMR spectra to fluorotrichloromethane, ¹¹B NMR spectra to the boron-trifluoride-diethyl-ether-complex, ³¹P NMR spectra to a 85% phosphoric(V) acid solution and ⁷Li NMR spectra to 9.7 M LiCl in D₂O. 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 MoKα radiation. The single crystals were mounted in perfluoroether oil on a MiTeGen Micromount™. B(Ohfip)₃ has CCSD deposition number 1004582 and the MeCN-adduct 1004583.

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**References**