


 Cite this: *Chem. Commun.*, 2025, 61, 10182

 Received 24th April 2025,  
Accepted 2nd June 2025

DOI: 10.1039/d5cc02299a

rsc.li/chemcomm

A  $^{19}\text{F}$  NMR spectroscopic probe, *p*-fluorobenzonitrile, is used to evaluate the relative Lewis acidity of boranes. The resulting scale is compared with the Gutmann–Beckett method which uses triethylphosphine oxide as a  $^{31}\text{P}$  NMR probe and both are compared to computed fluoride affinities.

Boranes are widely used Lewis acids in stoichiometric and catalytic transformations.<sup>1–18</sup> The Lewis acid strength is often correlated to reactivity, thus, relative Lewis acidity is valuable information for engineering reactions.<sup>19–30</sup> Boranes span diverse electronic and steric environments, dependent on their substitution, that presents challenges in achieving a universal Lewis acidity scale.<sup>31,32</sup>

Computed fluoride affinities (FAs), hydride affinities (HA), and LUMO energies are simple and effective indicators for analyzing the Lewis acidity of boranes.<sup>31,32</sup> Experimental methods are desired to compliment *in silico* data with common methods assessing the binding of a Lewis base probe to the borane by NMR,<sup>33–39</sup> IR,<sup>40–44</sup> absorption, or emission spectroscopy.<sup>45–49</sup> The Childs' method measures the  $^1\text{H}$  NMR chemical shift of the  $\gamma$ -proton of *trans*-crotonaldehyde upon coordination (Fig. 1).<sup>29,34,50</sup> The *trans*-crotonaldehyde probe is a Michael acceptor that is incompatible with many boranes by reaction, rather than coordination, and Greb recently demonstrated that *trans*-crotonaldehyde only gives reliable results for the strongest Lewis acids.<sup>51</sup> The Gutmann–Beckett method is the most widely adopted, that uses  $\text{OPET}_3$  as a probe where the Lewis acidity is assessed by measuring the difference in  $^{31}\text{P}$  NMR chemical shift between free  $\text{OPET}_3$  and its borane adduct ( $\Delta\delta$   $^{31}\text{P}$ , Fig. 1).<sup>52–56</sup> The  $\Delta\delta$   $^{31}\text{P}$  value for  $\text{BoCb}_3$  is 27.5 ppm but for  $\text{HB}^{\text{Me}}\text{oCb}_2$  is 30.0 ppm, contrary to the FA values of 605 and 527  $\text{kJ mol}^{-1}$ , respectively, as well as observed reactivity ( $\text{oCb}$  = *ortho*-carborane,  $^{\text{Me}}\text{oCb}$  = 1-methyl-*ortho*-carborane).<sup>57–59</sup>

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d5cc02299a>

## Müller versus Gutmann–Beckett for assessing the Lewis acidity of boranes†

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The discrepancy is attributed to the bulk of the  $\text{OPET}_3$  probe indicating the Gutmann–Beckett method can underestimate bulky Lewis acids as they make frustrated Lewis pairs.<sup>59,60</sup> Baumgartner and Caputo developed a fluorescence-based method for determining the strength of Lewis acids using a dithienophosphole oxide as a fluorescence probe (Fig. 1).<sup>45,61,62</sup> For this method, the probe is not commercially available, accurate fluorescence measurements require high sample purity, the Lewis acid cannot be a competing chromophore and must be stable at high dilutions, and strong Lewis acids require an instrument capable of near IR detection.<sup>45,61</sup> Lewis acid reactivity and catalysis is typically done in solution and most synthetic labs have access to NMR spectrometers, making NMR probes practical. From the aforementioned studies, the criteria for a useful experimental NMR spectroscopic Lewis acidity



Fig. 1 Spectroscopic probes for the determination of Lewis acidity of boranes.



probe are commercial availability, receptivity of the nucleus to NMR spectroscopy, a wide chemical shift range, and a small steric profile.

Recently, Müller and co-workers used 4-fluorobenzonitrile (FBN) as a probe to assess the Lewis acidity of intramolecularly stabilized silylium species by monitoring the change in chemical shift in the  $^{19}\text{F}$  NMR spectrum upon coordination (Fig. 2).<sup>37,63–66</sup> In their silylium study, the change in  $^{19}\text{F}$  NMR chemical shift upon coordination is consistent with the substituent's electronic effects on the Lewis acidity. This is an attractive probe as it is commercially available, the ease of  $^{19}\text{F}$  NMR spectroscopy and sensitivity of the nucleus, as well as wide chemical shift range. Inspired by Müller's study, we sought to determine if FBN would be an effective Lewis acidity probe for boranes.

The boranes selected were prominent Lewis acids that are commercially available as well as fluoroaryl and carborane systems as there were inconsistencies between Gutmann–Beckett values and the FAs. In the literature, it has been reported that NMR probe shifts can vary if there is an equilibrium, thus we conducted experiments with 3 equivalents of Lewis acid to favor complete binding of the probe.<sup>54,67</sup> The experiments for the Müller method were conducted by preparing a solution with a 1:3 molar ratio of FBN to borane in  $\text{CDCl}_3$  and the  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra were recorded at 23 °C using  $\text{PhCF}_3$  as an internal standard. The Müller method experiments were also conducted in 1:1 molar ratios in  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$  and showed identical scales indicating that the trend is not affected from switching from  $\text{CDCl}_3$  to  $\text{C}_6\text{D}_6$  (Fig. S1, ESI†). The  $\Delta\delta^{19}\text{F}$  value is the chemical shift difference between the adduct and free FBN ( $\Delta\delta^{19}\text{F} = \delta\text{FBN}\cdot\text{BR}_3 - \delta\text{FBN}$ ). In the literature, the majority of Gutmann–Beckett values are reported in  $\text{CD}_2\text{Cl}_2$ , however  $\text{CD}_2\text{Cl}_2$  has become heavily restricted.<sup>68,69</sup> Based on cost and availability,  $\text{CDCl}_3$  was selected as the solvent for all probe studies.

For the Gutmann–Beckett experiments, a similar procedure was conducted using  $\text{OPEt}_3$  as the NMR probe and  $^{31}\text{P}\{^1\text{H}\}$  spectroscopy. Calculations for gas phase fluoride affinities (FAs) were conducted using BPV86/SVP single point calculations. Percent buried volumes ( $\% V_{\text{Bur}}$ ) were calculated *via* the SambVca 2.1 tool on the respective fluoride adducts based on the method recently reported by Radius and Finze.<sup>31</sup> Some FAs and  $\% V_{\text{Bur}}$  had been reported previously which are in Table 1.<sup>31,32,57,58,70,71</sup> Müller had reported a  $\Delta\delta^{19}\text{F}$  for  $\text{B}(\text{C}_6\text{F}_5)_3$  in  $\text{CD}_2\text{Cl}_2$  of 10.9,<sup>37</sup> very close to the value we obtained in  $\text{CDCl}_3$  of 10.8 ppm. The  $\text{CDCl}_3$  values are represented in Table 1 with more detailed results in the ESI.† A scale for each



Fig. 2 Müller method for assessing the Lewis acidity of intramolecularly stabilized silylium cations using FBN as a  $^{19}\text{F}$  NMR probe.

Table 1 Müller ( $\delta^{19}\text{F}$  FBN =  $-102.42$ ), Gutmann–Beckett ( $\delta^{31}\text{P}$   $\text{OPEt}_3$  =  $52.3$ ), fluoride affinities (FA,  $\text{kJ mol}^{-1}$ ), and % buried volumes ( $\% V_{\text{Bur}}$ ). Chemical shifts in ppm, NR = no reaction

$\text{BR}_3$	$\delta\text{FBN}\cdot\text{BR}_3$	$\Delta\delta^{19}\text{F}$	$\Delta\delta^{31}\text{P}$	FA	$\% V_{\text{Bur}}$
$\text{BBr}_3$	$-89.21$	$13.2$	$35.9$	$443^{70}$	$43.0^{31}$
$\text{BCl}_3$	$-90.23$	$12.1$	$32.9$	$404^{70}$	$40.9^{31}$
$\text{Et}_2\text{O}\cdot\text{BF}_3$	NR	—	$26.1$	$338^{71}$	$33.3^{31}$
$\text{PhBBr}_2$	$-91.04$	$11.4$	$34.5$	$414$	$46.1$
$\text{Ph}_2\text{BBr}$	$-97.52$	$4.9$	$29.5$	$388$	$49.4$
$\text{BPh}_3$	NR	—	$4.8$	$342^{71}$	$53.1^{31}$
$\text{PhBCl}_2$	$-98.25$	$4.2$	$31.4$	$385$	$44.7$
$\text{B}(\text{OMe})_3$	NR	—	NR	$233$	$44.2$
$\text{HB}(\text{C}_6\text{F}_5)_2$	$-93.04$	$9.4$	$28.6$	$417^{58}$	$47.0^{32}$
$\text{B}(\text{C}_6\text{F}_5)_3$	$-91.59$	$10.8$	$23.6$	$449^{57}$	$58.9^{32}$
$\text{Br}^{\text{Ph}}\text{oCb}_2$	$-88.74$	$13.7$	$31.2$	$524$	$74.8$
$\text{Br}^{\text{Me}}\text{oCb}_2$	$-87.74$	$14.7$	$33.9$	$548$	$69.4$
$\text{HB}^{\text{Me}}\text{oCb}_2$	$-90.59$	$11.8$	$30.2$	$527^{58}$	$64.7^{58}$
$\text{BoCb}_3$	$-87.35$	$15.1$	$27.6$	$605^{57}$	$71.9^{32}$

of the methods was made based on the experiments and calculations, depicted in Fig. 3.

Adduct formation for either probe, or thermodynamically favored energies for fluoride binding, was not observed for  $\text{B}(\text{OMe})_3$ . For  $\text{BPh}_3$ , a  $\Delta\delta^{31}\text{P}$  value of 4.8 ppm and for  $\text{Et}_2\text{O}\cdot\text{BF}_3$ , a value of 26.1 ppm were obtained but no FBN binding. This indicates that all three methods do not give results for weak Lewis acids.

The fluoride affinity scale gave the trend of:  $\text{BoCb}_3 > \text{Br}^{\text{Me}}\text{oCb}_2 > \text{HB}^{\text{Me}}\text{oCb}_2 > \text{Br}^{\text{Ph}}\text{oCb}_2 > \text{B}(\text{C}_6\text{F}_5)_3 > \text{BBr}_3 > \text{HB}(\text{C}_6\text{F}_5)_2 > \text{PhBBr}_2 > \text{BCl}_3 > \text{Ph}_2\text{BBr} > \text{PhBCl}_2 > \text{BPh}_3 > \text{Et}_2\text{O}\cdot\text{BF}_3 > \text{B}(\text{OMe})_3$ . The Gutmann–Beckett scale followed the trend:  $\text{BBr}_3 > \text{PhBBr}_2 > \text{Br}^{\text{Me}}\text{oCb}_2 > \text{BCl}_3 > \text{PhBCl}_2 > \text{Br}^{\text{Ph}}\text{oCb}_2 > \text{HB}^{\text{Me}}\text{oCb}_2 > \text{Ph}_2\text{BBr} > \text{HB}(\text{C}_6\text{F}_5)_2 > \text{BoCb}_3 > \text{Et}_2\text{O}\cdot\text{BF}_3 > \text{B}(\text{C}_6\text{F}_5)_3 > \text{BPh}_3$ . Lastly, the Müller values gave the trend of:  $\text{BoCb}_3 > \text{Br}^{\text{Me}}\text{oCb}_2 > \text{Br}^{\text{Ph}}\text{oCb}_2 > \text{BBr}_3 > \text{BCl}_3 > \text{HB}^{\text{Me}}\text{oCb}_2 > \text{PhBBr}_2 > \text{B}(\text{C}_6\text{F}_5)_3 > \text{HB}(\text{C}_6\text{F}_5)_2 > \text{Ph}_2\text{BBr} > \text{PhBCl}_2$ .

In the perfluorophenyl species, the Gutmann–Beckett method has  $\text{B}(\text{C}_6\text{F}_5)_3$  weaker than Piers' borane ( $\text{HB}(\text{C}_6\text{F}_5)_2$ ) with both being weaker than  $\text{BCl}_3$  while the FA values are inverted and match with the substituent's electron withdrawing effects. The Gutmann–Beckett value for  $\text{BoCb}_3$  is between  $\text{B}(\text{C}_6\text{F}_5)_3$  and Piers' borane while the FAs indicate that it is the strongest Lewis acid. The bis(carboranyl)boranes ( $\text{Br}^{\text{Me}}\text{oCb}_2$ ,  $\text{HB}^{\text{Me}}\text{oCb}_2$ , and  $\text{Br}^{\text{Ph}}\text{oCb}_2$ ) are sequentially lower by FA than  $\text{BoCb}_3$  while the Gutmann–Beckett values indicate  $\text{BBr}_3$  is stronger and  $\text{BCl}_3$  is between  $\text{Br}^{\text{Me}}\text{oCb}_2$  and  $\text{Br}^{\text{Ph}}\text{oCb}_2$ . The Gutmann–Beckett values are not in very good agreement with FAs for the bulky systems but does order the smaller boranes the same as FAs ( $\text{BBr}_3$ ,  $\text{PhBBr}_2$ ,  $\text{BCl}_3$ ,  $\text{Ph}_2\text{BBr}$ ,  $\text{PhBCl}_2$ ) with the exception of  $\text{Ph}_2\text{BBr}$  being switched with  $\text{PhBCl}_2$  but their FAs only differ by 3  $\text{kJ mol}^{-1}$ . In comparing the FA values





Fig. 3 (a) The fluoride affinity scale, (b) Gutmann–Beckett scale, and (c) Müller method scale.

to the Müller values, there is better agreement between the two scales than the Gutmann–Beckett.

The Pearson correlation coefficient for the Gutmann–Beckett values compared to the FA values is 0.36, indicating moderate correlation between them. The corresponding Pearson correlation coefficient for the Müller values indicates a strong positive correlation to FAs with a coefficient of 0.76. In the FA and Müller scales, the strongest Lewis acid is  $\text{B}\cdot\text{OCb}_3$  followed by  $\text{BrB}^{\text{Me}}\text{oCb}_2$ . For the secondary carboranyl boranes, the FAs indicate  $\text{BrB}^{\text{Me}}\text{oCb}_2 > \text{HB}^{\text{Me}}\text{oCb}_2 > \text{BrB}^{\text{Ph}}\text{oCb}_2$  while the Müller values indicate  $\text{BrB}^{\text{Me}}\text{oCb}_2 > \text{BrB}^{\text{Ph}}\text{oCb}_2 > \text{HB}^{\text{Me}}\text{oCb}_2$ , but the FAs of  $\text{BrB}^{\text{Ph}}\text{oCb}_2$  and  $\text{HB}^{\text{Me}}\text{oCb}_2$  only differ by  $3 \text{ kJ mol}^{-1}$  indicating the discrepancy is for close values. The weakest two Lewis acids,  $\text{Ph}_2\text{BBr}$  and  $\text{PhBCl}_2$ , are in the same order for FA and the Müller values. Both methods order  $\text{B}(\text{C}_6\text{F}_5)_3$  as stronger than  $\text{HB}(\text{C}_6\text{F}_5)_2$ . In the small boranes ( $\text{BBR}_3$ ,  $\text{PhBBR}_2$ ,  $\text{BCl}_3$ ,  $\text{Ph}_2\text{BBr}$ , and  $\text{PhBCl}_2$ ), the only ordering difference is  $\text{BCl}_3$  and  $\text{PhBBR}_2$ , but as with the other errors, the FAs differ by only  $10 \text{ kJ mol}^{-1}$ . In general, the Müller and Gutmann–Beckett scales are in similar agreement with FAs for the smaller boranes, however for the bulkier Lewis acids, the Müller method prevails.

In conclusion, the  $^{19}\text{F}$  NMR spectroscopic 4-fluorobenzenitrile probe or Müller method gives a scale that is in good agreement with FAs and the substituents' electron withdrawing influence on Lewis acidity. This is regardless of bulk on the Lewis acid that is attributed to the minimal steric profile of the linear nitrile group. The Gutmann–Beckett method gave values consistent with FAs for small boranes, but did not have results in agreement with FAs for boranes bearing bulky pentafluorophenyl groups or carborane substituents. Researchers are urged to use the Gutmann–Beckett method with caution for bulky systems. A limitation of the Müller method is that it is not effective for weak Lewis acids, but this is also the case for FAs

and to a lesser extent, the Gutmann–Beckett method. The commercial availability, operational simplicity of the  $^{19}\text{F}$  NMR spectroscopic probe makes the Müller method attractive to use to assess relative Lewis acidity. Collectively, our results indicate that FBN is an effective probe to evaluate the relative Lewis acidity of boranes, regardless of steric bulk.

S. R., Y. L., M. E. A., and M. O. A. designed and carried out the laboratory experiments under consultation and supervision from C. D. M. R. A. T. performed the DFT calculations. All authors analyzed the results and contributed to the composition of the manuscript.

We are grateful to the Welch Foundation (Grant No. 2203-20240404 an X-AA-0002-20230731) and the National Science Foundation (Award No. 2349851) for their generous support of this work. We thank the reviewers for their valuable suggestions that improved this manuscript.

## Data availability

The following files are available free of charge. Experimental details, NMR spectra and the DFT calculations.

## Conflicts of interest

There are no conflicts to declare.

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