ChemComm

Check for updates

Cite this: Chem. Commun., 2025.

Received 24th April 2025,

Accepted 2nd June 2025 DOI: 10.1039/d5cc02299a

rsc.li/chemcomm

61, 10182



View Article Online

View Journal | View Issue

COMMUNICATION

Müller *versus* Gutmann–Beckett for assessing the Lewis acidity of boranes[†]

Sameera Ranasinghe, Yijie Li, D Madison E. Andrews, Manjur O. Akram, Ragene A. Thornton and Caleb D. Martin *

A ¹⁹F 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 ³¹P NMR probe and both are compared to computed fluoride affinities.

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

Computed fluoride affinities (FAs), hydride affinities (HA), and LUMO energies are simple and effective indicators for analyzing the Lewis acidity of boranes.^{31,32} 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,³³⁻³⁹ IR,⁴⁰⁻⁴⁴ absorption, or emission spectroscopy.⁴⁵⁻⁴⁹ The Childs' method measures the ¹H NMR chemical shift of the γ -proton of *trans*-crotonaldehyde upon coordination (Fig. 1).^{29,34,50} 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.⁵¹ The Gutmann-Beckett method is the most widely adopted, that uses OPEt₃ as a probe where the Lewis acidity is assessed by measuring the difference in ³¹P NMR chemical shift between free OPEt₃ and its borane adduct ($\Delta \delta^{31}$ P, Fig. 1).⁵²⁻⁵⁶ The $\Delta \delta^{31}$ P value for BoCb₃ is 27.5 ppm but for HB^{Me}oCb₂ is 30.0 ppm, contrary to the FA values of 605 and 527 kJ mol⁻¹, respectively, as well as observed reactivity $(oCb = ortho-carborane, {}^{Me}oCb = 1-methyl-ortho-carborane).^{57-59}$

The discrepancy is attributed to the bulk of the OPEt₃ probe indicating the Gutmann–Beckett method can underestimate bulky Lewis acids as they make frustrated Lewis pairs.^{59,60} 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).^{45,61,62} 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.^{45,61} 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.

Department of Chemistry and Biochemistry, Baylor University, One Bear Place #97348, Waco, TX 76798, USA. E-mail: caleb d martin@baylor.ed

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

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 ¹⁹F NMR spectrum upon coordination (Fig. 2).^{37,63–66} In their silylium study, the change in ¹⁹F 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 ¹⁹F 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.54,67 The experiments for the Müller method were conducted by preparing a solution with a 1:3 molar ratio of FBN to borane in CDCl₃ and the ${}^{19}F{}^{1}H{}$ NMR spectra were recorded at 23 °C using PhCF₃ as an internal standard. The Müller method experiments were also conducted in 1:1 molar ratios in CDCl3 and C6D6 and showed identical scales indicating that the trend is not affected from switching from CDCl₃ to C₆D₆ (Fig. S1, ESI[†]). The $\Delta \delta$ ¹⁹F 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 CD₂Cl₂, however CD₂Cl₂ has become heavily restricted.^{68,69} Based on cost and availability, CDCl₃ was selected as the solvent for all probe studies.

For the Gutmann–Beckett experiments, a similar procedure was conducted using OPEt₃ as the NMR probe and ³¹P{¹H} spectroscopy. Calculations for gas phase fluoride affinities (FAs) were conducted using BPV86/SVP single point calculations. Percent buried volumes (% V_{Bur}) were calculated *via* the SambVca 2.1 tool on the respective fluoride adducts based on the method recently reported by Radius and Finze.³¹ Some FAs and % V_{Bur} had been reported previously which are in Table 1.^{31,32,57,58,70,71} Müller had reported a $\Delta \delta$ ¹⁹F for B(C₆F₅)₃ in CD₂Cl₂ of 10.9,³⁷ very close to the value we obtained in CDCl₃ of 10.8 ppm. The CDCl₃ 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 ¹⁹F NMR probe.

Table 1	Müller (δ^{19} F F	BN = -1	.02.42),	Gutm	nann–Bec	kett (δ^{31} P	OF	Et ₃ =
52.3), flu	oride affinities	(FA, kJ	mol^{-1}),	and	% buried	volumes	(%	V _{Bur}).
Chemica	al shifts in ppm,	NR = nc	o reactic	n				

R,	:N=	R <mark>-B</mark> +−∹N R	I≡−∕	F oCb: №oC PhoC	R^1 $R^1 = H$ $b: R^1 = CH_3$ $b: R^1 = Ph$ = BH
BR ₃	$\delta FBN \cdot BR_3$	$\Delta \delta \ ^{19}{\rm F}$	$\Delta \delta$ $^{31}{ m P}$	FA	% V _{Bur}
BCl ₃ Et ₂ O·BF ₃ PhBBr ₂ Ph ₂ BBr BPh ₃ PhBCl ₂ B(OMe) ₃ HB(C ₆ F ₅) ₂	-90.23 NR -91.04 -97.52 NR -98.25 NR -93.04 -91.59	$ \begin{array}{c} 12.1 \\ - \\ 11.4 \\ 4.9 \\ - \\ 4.2 \\ - \\ 9.4 \\ 10.8 \end{array} $	32.9 26.1 34.5 29.5 4.8 31.4 NR 28.6 23.6	$\begin{array}{c} 404^{70} \\ 338^{71} \\ 414 \\ 388 \\ 342^{71} \\ 385 \\ 233 \\ 417^{58} \\ 449^{57} \end{array}$	$\begin{array}{c} 40.9^{31} \\ 33.3^{31} \\ 46.1 \\ 49.4 \\ 53.1^{31} \\ 44.7 \\ 44.2 \\ 47.0^{32} \\ 58.0^{32} \end{array}$
$ \begin{array}{c} B(C_{6}r_{5})_{3} \\ BrB^{Ph}oCb_{2} \\ BrB^{Me}oCb_{2} \\ HB^{Me}oCb_{2} \\ BoCb_{3} \end{array} $	-91.39 -88.74 -87.74 -90.59 -87.35	10.8 13.7 14.7 11.8 15.1	23.6 31.2 33.9 30.2 27.6	524 548 527 ⁵⁸ 605 ⁵⁷	58.974.869.464.75871.932

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 $B(OMe)_3$. For BPh₃, a $\Delta\delta$ ³¹P value of 4.8 ppm and for Et₂O·BF₃, 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: BoCb₃ > BrB^{Me}oCb₂ > HB^{Me}oCb₂ > BrB^{Ph}oCb₂ > B(C₆F₅)₃ > BBr₃ > HB(C₆F₅)₂ > PhBBr₂ > BCl₃ > Ph₂BBr > PhBCl₂ > BPh₃ > Et₂O·BF₃ > B(OMe)₃. The Gutmann–Beckett scale followed the trend: BBr₃ > PhBBr₂ > BrB^{Me}oCb₂ > BCl₃ > PhBCl₂ > BrB^{Ph}oCb₂ > HB^{Me}oCb₂ > Ph₂BBr > HB(C₆F₅)₂ > BoCb₃ > Et₂O·BF₃ > B(C₆F₅)₃ > BPh₃. Lastly, the Müller values gave the trend of: BoCb₃ > BrB^{Me}oCb₂ > BrB^{Ph}oCb₂ > BBr₃ > BCl₃ > HB^{Me}oCb₂ > PhBBr₂ > B(C₆F₅)₃ > HB(C₆F₅)₂ > Ph₂BBr > PhBCl₂.

In the perfluorophenyl species, the Gutmann–Beckett method has $B(C_6F_5)_3$ weaker than Piers' borane $(HB(C_6F_5)_2)$ with both being weaker than BCl_3 while the FA values are inverted and match with the substituent's electron withdrawing effects. The Gutmann–Beckett value for $BoCb_3$ is between $B(C_6F_5)_3$ and Piers' borane while the FAs indicate that it is the strongest Lewis acid. The bis(carboranyl)boranes $(BrB^{Me}oCb_2, HB^{Me}oCb_2, and BrB^{Ph}oCb_2)$ are sequentially lower by FA than $BoCb_3$ while the Gutmann–Beckett values indicate BBr_3 is stronger and BCl_3 is between $BrB^{Me}oCb_2$ and $BrB^{Ph}oCb_2$. 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 $(BBr_3, PhBBr_2, BCl_3, Ph_2BBr, PhBCl_2)$ with the exception of Ph_2BBr being switched with PhBCl₂ but their FAs only differ by 3 kJ mol⁻¹. In comparing the FA values



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 BoCb₃ followed by BrB^{Me}oCb₂. For the secondary carboranyl boranes, the FAs indicate $BrB^{Me}oCb_2 > HB^{Me}oCb_2 > BrB^{Ph}oCb_2$ while the Müller values indicate $BrB^{Me}oCb_2 > BrB^{Ph}oCb_2 > HB^{Me}oCb_2$, but the FAs of BrB^{Ph}oCb₂ and HB^{Me}oCb₂ only differ by 3 kJ mol⁻¹ indicating the discrepancy is for close values. The weakest two Lewis acids, Ph2BBr and PhBCl2, are in the same order for FA and the Müller values. Both methods order $B(C_6F_5)_3$ as stronger than HB(C₆F₅)₂. In the small boranes (BBr₃, PhBBr₂, BCl₃, Ph₂BBr, and PhBCl₂), the only ordering difference is BCl₃ and PhBBr₂, but as with the other errors, the FAs differ by only 10 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 ¹⁹F NMR spectroscopic 4-fluoroben zonitrile 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 ¹⁹F 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.

References

- 1 L. Deloux and M. Srebnik, Chem. Rev., 1993, 93, 763-784.
- 2 W. E. Piers and T. Chivers, Chem. Soc. Rev., 1997, 26, 345-354.
- 3 W. Piers, *Advances in Organometallic Chemistry*, Academic Press Cambridge, MA, USA, 2004.
- 4 G. Erker, Dalton Trans., 2005, 1883–1890.
- 5 D. W. Stephan, Catal. Precious Met., 2010, 261-275.
- 6 D. W. Stephan and G. Erker, Angew. Chem., Int. Ed., 2010, 49, 46-76.

- 7 R. L. Melen, Chem. Commun., 2014, 50, 1161-1174.
- 8 D. W. Stephan, Acc. Chem. Res., 2015, 48, 306-316.
- 9 D. W. Stephan and G. Erker, Angew. Chem., Int. Ed., 2015, 54, 6400-6441.
- 10 D. W. Stephan, J. Am. Chem. Soc., 2015, 137, 10018-10032.
- 11 M. Hatano and K. Ishihara, Lewis Acids, *Boron Reagents in Synthesis*, American Chemical Society, 2016, vol. 1236, pp. 27–66.
- 12 J. W. Fyfe and A. J. Watson, Chem, 2017, 3, 31–55.
- 13 J. R. Lawson and R. L. Melen, Inorg. Chem., 2017, 56, 8627-8643.
- 14 B. Rao and R. Kinjo, Chem. Asian J., 2018, 13, 1279-1292.
- 15 D. Willcox and R. L. Melen, Trends Chem., 2019, 1, 625-626.
- 16 J. L. Carden, A. Dasgupta and R. L. Melen, *Chem. Soc. Rev.*, 2020, **49**, 1706–1725.
- 17 E. A. Patrick and W. E. Piers, Chem. Commun., 2020, 56, 841-853.
- 18 V. Nori, F. Pesciaioli, A. Sinibaldi, G. Giorgianni and A. Carlone, *Catalysts*, 2022, **12**, 5.
- 19 M. A. Beckett, G. C. Strickland, J. R. Holland and K. S. Varma, *Polym. J.*, 1996, 37, 4629–4631.
- 20 D. J. Morrison and W. E. Piers, Org. Lett., 2003, 5, 2857-2860.
- 21 I. B. Sivaev and V. I. Bregadze, Coord. Chem. Rev., 2014, 270-271, 75-88.
- 22 G. G. Briand, S. A. Cairns, A. Decken, C. M. Dickie, T. I. Kostelnik and M. P. Shaver, *J. Organomet. Chem.*, 2016, **806**, 22–32.
- 23 W. Li and T. Werner, Org. Lett., 2017, 19, 2568-2571.
- 24 L. Süsse, M. Vogler, M. Mewald, B. Kemper, E. Irran and M. Oestreich, *Angew. Chem., Int. Ed.*, 2018, **57**, 11441–11444.
- 25 G. G. Briand, A. Decken, W. E. M. M. Shannon and E. E. Trevors, *Can. J. Chem.*, 2018, 96, 561–569.
- 26 A. Brar, D. K. Unruh, N. Ling and C. Krempner, *Org. Lett.*, 2019, **21**, 6305–6309.
- 27 K. A. Andrea and F. M. Kerton, ACS Catal., 2019, 9, 1799-1809.
- 28 A. J. Woodside, M. A. Smith, T. M. Herb, B. C. Manor, P. J. Carroll, P. R. Rablen and C. R. Graves, *Organometallics*, 2019, 38, 1017–1020.
- 29 R. J. Mayer, N. Hampel and A. R. Ofial, Chem. Eur. J., 2021, 27, 4070-4080.
- 30 J. Wang and Q. Ye, Chem. Eur. J., 2024, 30, e202303695.
- 31 L. Zapf, M. Riethmann, S. A. Föhrenbacher, M. Finze and U. Radius, *Chem. Sci.*, 2023, 14, 2275–2288.
- 32 M. O. Akram, C. D. Martin and J. L. Dutton, *Inorg. Chem.*, 2023, **62**, 13495–13504.
- 33 J. F. Deters, P. A. McCusker and R. C. PilgerJr, J. Am. Chem. Soc., 1968, 90, 4583–4585.
- 34 R. F. Childs, D. L. Mulholland and A. Nixon, *Can. J. Chem.*, 1982, **60**, 801–808.
- 35 A. Zheng, S.-B. Liu and F. Deng, Chem. Rev., 2017, 117, 12475–12531.
- 36 J. J. Jennings, B. W. Wigman, B. M. Armstrong and A. K. Franz, J. Org. Chem., 2019, 84, 15845–15853.
- 37 S. Künzler, S. Rathjen, A. Merk, M. Schmidtmann and T. Müller, *Chem. – Eur. J.*, 2019, 25, 15123–15130.
- 38 J. Ramler and C. Lichtenberg, *Chem. Eur. J.*, 2020, 26, 10250–10258.
 39 K. K. Samudrala, M. O. Akram, J. L. Dutton, C. D. Martin and
- M. P. Conley, *Inorg. Chem.*, 2024, **63**, 4939–4946.
- 40 M. Lappert, J. Am. Chem. Soc., 1961, 817-822.
- 41 M. Lappert, J. Am. Chem. Soc., 1962, 542-548.
- 42 C. S. Hanson, M. C. Psaltakis, J. J. Cortes, S. S. Siddiqi and J. J. DeveryIII, J. Org. Chem., 2019, 85, 820–832.
- 43 M. Ravi, V. L. Sushkevich and J. A. van Bokhoven, *Nat. Mater.*, 2020, **19**, 1047–1056.
- 44 M. A. Kostin, S. A. Pylaeva and P. M. Tolstoy, *Phys. Chem. Chem. Phys.*, 2022, 24, 7121-7133.

- 45 J. R. Gaffen, J. N. Bentley, L. C. Torres, C. Chu, T. Baumgartner and C. B. Caputo, *Chem*, 2019, 5, 1567–1583.
- 46 S. Fukuzumi and K. Ohkubo, J. Am. Chem. Soc., 2002, 124, 10270-10271.
- 47 C. S. Branch, S. G. Bott and A. R. Barron, *J. Organomet. Chem.*, 2003, 666, 23-34.
- 48 K. Ohkubo, S. C. Menon, A. Orita, J. Otera and S. Fukuzumi, J. Org. Chem., 2003, 68, 4720–4726.
- 49 C. Goonesinghe, H.-J. Jung, I. O. Betinol, J. R. Gaffen, C. N. Garrard, J. Chang, K. Hosseini, H. Roshandel, K. Nyamayaro and B. Patrick, *ACS Catal.*, 2023, **13**, 16148–16157.
- 50 G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei and D. W. Stephan, *Dalton Trans.*, 2007, 3407–3414.
- 51 P. Erdmann, M. Schmitt, L. Janus and L. Greb, *Chem. Eur. J.*, 2025, **31**, e202404181.
- 52 U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 1235–1257.
- 53 C. Zhang, J. Wang, W. Su, Z. Lin and Q. Ye, *J. Am. Chem. Soc.*, 2021, 143, 8552–8558.
- 54 P. Erdmann and L. Greb, Angew. Chem., Int. Ed., 2022, 61, e202114550.
- 55 C. Zhang, X. Liu, J. Wang and Q. Ye, Angew. Chem., Int. Ed., 2022, 61, e202205506.
- 56 Y. Wei, J. Wang, W. Yang, Z. Lin and Q. Ye, *Chem. Eur. J.*, 2023, 29, e202203265.
- 57 M. O. Akram, J. R. Tidwell, J. L. Dutton and C. D. Martin, Angew. Chem., Int. Ed., 2022, 61, e202212073.
- 58 M. O. Akram, J. R. Tidwell, J. L. Dutton and C. D. Martin, Angew. Chem., Int. Ed., 2023, 62, e202307040.
- 59 K. Vashisth, S. Dutta, M. O. Akram and C. D. Martin, *Dalton Trans.*, 2023, **52**, 9639–9645.
- 60 L. Xiang, J. Wang, A. Matler and Q. Ye, Chem. Sci., 2024, 15, 17944-17949.
- 61 J. N. Bentley, S. A. Elgadi, J. R. Gaffen, P. Demay-Drouhard, T. Baumgartner and C. B. Caputo, *Organometallics*, 2020, 39, 3645–3655.
- 62 A. E. Laturski, J. R. Gaffen, P. Demay-Drouhard, C. B. Caputo and T. Baumgartner, *Precis. Chem.*, 2023, **1**, 49–56.
- 63 A. Schäfer, M. R. Mann, A. Schäfer, W. Saak, D. Haase and T. Müller, Angew. Chem., Int. Ed., 2011, **50**, 12636–12638.
- 64 H. Großekappenberg, M. R. Mann, M. Schmidtmann and T. Müller, Organometallics, 2015, 34, 4952–4958.
- 65 N. Kordts, S. Künzler, S. Rathjen, T. Sieling, H. Großekappenberg, M. Schmidtmann and T. Müller, *Chem. – Eur. J.*, 2017, 23, 10068–10079.
- 66 S. Künzler, S. Rathjen, K. Rüger, M. S. Würdemann, M. Wernke, P. Tholen, C. Girschik, M. Schmidtmann, Y. Landais and T. Müller, *Chem. – Eur. J.*, 2020, 26, 16441–16449.
- 67 M. Yang, D. Tofan, C.-H. Chen, K. M. Jack and F. P. Gabbaï, *Angew. Chem., Int. Ed.*, 2018, 57, 13868–13872.
- 68 P. M. Schlosser, A. S. Bale, C. F. Gibbons, A. Wilkins and G. S. Cooper, *Environ. Health Perspect.*, 2015, **123**, 114–119.
- 69 O. Singh and V. K. Singh, *Hazardous Chemicals*, Elsevier, 2025, pp. 305–313.
- 70 L. O. Müller, D. Himmel, J. Stauffer, G. Steinfeld, J. Slattery, G. Santiso-Quiñones, V. Brecht and I. Krossing, *Angew. Chem., Int.* Ed., 2008, 47, 7659–7663.
- 71 I. Krossing and I. Raabe, Chem. Eur. J., 2004, 10, 5017-5030.