

Illuminating Lewis acidity strength

Darren Willcox^a and Rebecca L. Melen^{a*}

Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, Cymru/Wales, UK

*Correspondence: MelenR@cardiff.ac.uk

Summary: In this issue of *Chem.* Baumgartner, Caputo and co-workers describe a simple naked eye litmus test for the determination of Lewis acid strength. This technique is based on fluorescence using highly tunable, luminescent phosphole oxide Lewis basic probes.

Body: Lewis acids, compounds capable of accepting a pair of electrons, have become one of the most widely applied classes of reagents in chemistry with applications ranging from catalysis to materials. Lewis acids (LAs) can be either atomic or molecular species possessing a localized low-lying unoccupied orbital in which the electron density can be accommodated. This low-lying orbital means they readily react with Lewis bases (LBs, electron donors) to form Lewis adducts ($LA + LB \rightarrow LA \rightarrow LB$) through the sharing of the electron pair thus lowering its energy. This facile ability to form Lewis pairs has enabled methods allowing for the strength of the Lewis acid to be determined. Baumgartner, Caputo and co-workers¹ report a simple, straightforward and powerful method for determining Lewis acid strengths: a method which overcomes restrictive measurement parameters, strong Lewis base dependences and negates the requirement for complex experimental setups.

The past 20 years have witnessed remarkable discoveries that have greatly advanced the synthetic use of organo-main-group Lewis acid catalysis, namely frustrated Lewis pairs (FLPs).² With such a burgeoning field, assessment of the acceptor ability of Lewis acids has become of paramount importance, as this enables the end user to tune the chemical and functional utility of the catalyst. The determination of Lewis acidity can be classified into three main categories: effective, global and intrinsic metrics.³ Effective metrics are spectroscopic methods which measure the effect of the Lewis acid on a probe molecule (Figure 1). The most common examples include 1) the Gutmann-Beckett (GB) method⁴ – which involves the coordination of a probe, typically triethylphosphine oxide (Et_3PO), to a Lewis acid and recording the change in ^{31}P NMR resonance. The Lewis basic oxygen atom of Et_3PO can form an adduct with the Lewis acid, causing a de-shielding of the adjacent phosphorus atom, the degree of which can be measured to ascertain the Lewis acidity. b) The Childs method⁵ – which correlates the Lewis acidity by measuring the difference in 1H NMR resonances of the Lewis-pair against crotonaldehyde. Global metrics, on the other hand, consider the whole process of adduct formation and gives thermodynamic output such as intramolecular coordination in the initial Lewis acid (E_{intra}), deformation energies and preorganization (E_{prep}) in addition to the immediate interaction energy (E_{inter}). The common example of this technique is the fluoride ion affinities (FIA) method⁶ which calculates the change in enthalpy upon coordination of a fluoride anion to the Lewis acid based on the equation $LA + F^- \rightarrow LAF^-$. This technique can be regarded less as a measure of Lewis acidity but rather fluoridophilicity. The final class is intrinsic metrics, these probe the electronic structure of the free Lewis acid through a combination of quantum theoretical numbers or spectroscopy in a non-invasive fashion such that the Lower LUMO levels of the Lewis acid generally correspond to higher affinities. The main approach utilized for this technique is the Global Electrophilicity Index (GEI)⁷ which is based on the propensity of a molecule to take up electrons, and as such, the ranking of Lewis acidities is not defined with respect to a specific base. Despite the widespread use of these techniques to gain an

estimate of the Lewis acidity, they do exhibit limitations such as inconclusive results, constrained measurement parameters, non-quantitative results and complex experimental or DFT expensive setups.

Baumgartner, Caputo and co-workers have developed a simple, naked-eye litmus test which allows the determination of the Lewis acid strength through the generation of fluorescent Lewis adducts (FLAs). These FLAs exhibit distinct fluorescence and coloration profiles compared to the fluorescent phosphole oxide probe. While attempts have been made previously to use photophysical tests as a measure of Lewis acidity, no clear correlation between Lewis acidity and emission wavelength could be obtained.⁸ Central to the success of Baumgartner, Caputo and co-workers' approach is the choice of fluorescent phosphole oxide probe employed. The authors utilize dithienophosphole oxides where the optical properties can be fine-tuned effectively, particularly through extended conjugation. These dithienophosphole oxides are successful probes as complexation of a Lewis acid causes varying degrees of polarization of the P=O bond depending upon the strength of the Lewis acid. A strong Lewis acid would considerably increase the polarity of the P=O bond and thus increase the formal electronegativity of the oxygen, this in turn decreases the energy of the LUMO resulting in a red-shifted emission. To demonstrate the synthetic utility of this fluorescence-based Lewis acidity determination method, this work subjected a range of commonly employed main-group and transition-metal Lewis acids which contained differing sizes, steric bulk and charges. The emission spectra for the fluorescent Lewis adducts indicated a strong correlation between Lewis acidity and bathochromic shift shifts observed. From these results it was indicated that triphenylborane (BPh₃) was the weakest Lewis acid whereas the tritylium (Ph₃C⁺) and silylium (Et₃Si⁺) cations were the strongest in the series examined. From this data, after mathematical manipulation of both the Lewis bases and FLAs, the strength of the Lewis acid can be quantified. Moreover, the authors demonstrate that these dithienophosphole oxide probes can be used for multinuclear NMR analysis of the FLAs, analogous to the Guttmann-Beckett, with noticeable changes in the ³¹P{¹H} NMR resonances upon coordination to a Lewis acid.

Taken together, this method allows easy quantification of a wide range of Lewis acids under conditions relevant to their utility on a time scale which is comparable to the other widely utilized methods. This is a major step forward in addressing the experimental pitfalls that are commonplace with both the widely used experimental and theoretical techniques.

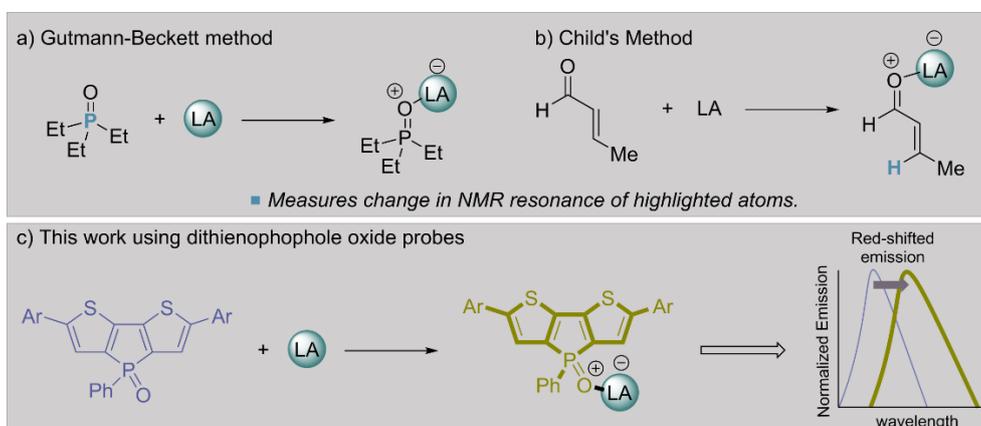


Figure 1. Methods of measuring Lewis acidity. (a) Gutmann-Beckett, (b) Childs, (c) this work using a dithienophosphole oxide probe.

Acknowledgments: We would like to thank the Leverhulme Trust (RPG-2016-020) and EPSRC for funding (EP/R026912/1).

References:

- 1 Graffen, J.R., Bentley, J.N., Torres, L.C., Chu, C., Baumgartner, T., Caputo C.B. (2019). A simple and effective method of Determining Lewis Acidity Using Fluorescence, CHEM, DOI:
- 2 Stephan, D.W. (2016). The broadening reach of frustrated Lewis pair chemistry, *Science*, 354, aaf7229.
- 3 Greb, L. (2018). Lewis Superacids: Classifications, Candidates, and Applications, *Chem. Eur. J.*, 24, 17881–17896.
- 4 Beckett, M.A., Strickland, G.C., Holland, J.R., Varma, J.S. (1996). A convenient n.m.r. method for the measurement of Lewis acidity at boron centres: correlation of reaction rates of Lewis acid initiated epoxide polymerizations with Lewis acidity. *Polymer*, 37, 4629–4631.
- 5 Childs, R.F., Mulholland, D.L., Nixon, A. (1982). The Lewis acid complexes of α,β -unsaturated carbonyl and nitrile compounds. A nuclear magnetic resonance study. *Can. J. Chem.*, 60, 801–808.
- 6 Christe, K.O., Dixon, D.A., McLemore, D., Wilson, W.W., Sheehy, J.A., Boatz, J.A. (2000). On a quantitative scale for Lewis acidity and recent progress in polynitrogen chemistry. *J. Fluorine Chem.*, 101, 151–153.
- 7 Jupp, A.R., Johnstone, T.C., Stephan, D.W. (2018). The global electrophilicity index as a metric for Lewis acidity. *Dalton Trans.*, 47, 7029–7035.
- 8 Soltani, Y., Adams, S.J., Börger, J., Wilkins, L.C., Newman, P.D., Pope, S.J.A., Melen, R.L. (2018). Synthesis and photophysical properties of imine borane adducts towards vapochromic materials. *Dalton Trans.*, 47, 12656–12660.