

## Review

## Lewis acidity of boron compounds



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## ABSTRACT

The effects of different electronic and structural factors in determining the Lewis acidity of boron compounds are analyzed. Scales of Lewis acidity for boron Lewis acids based on the Gutmann–Beckett and Childs methods have been constructed using data available in the literature. The Lewis acidities of transient boron Lewis acids have been estimated and their high Lewis acidity has been confirmed.

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## 1. Introduction

Acidity and basicity belong to the most important concepts in chemistry. There are several different definitions of acids and bases available. However, in Lewis theory they are specified in the most general terms as electron pair-acceptors and electron pair-donors, respectively [1]. The importance of the Lewis conceptual approach is rooted in the fact that it can be applied to compounds not containing protons. Borane derivatives represent Lewis acids par excellence owing to the electron deficiency of the central boron atom with a vacant p-orbital (Chart 1). The borane-based Lewis acids play key roles as catalysts in organic synthesis [2–5], activators for olefin polymerization organometallic pre-catalysts [6–8] and components of frustrated Lewis pairs (FLP) that promote activation of dihydrogen and other small molecules [9–13]. The change in Lewis acidity of boron compounds is the base of the design of fluorescent sensors for detection and recognition of carbohydrates and medications [14–18] as well as sensors for detection of fluoride and cyanide anions [18–20]. The Lewis acidity of boron compounds

plays an important role in mechanism of pharmacological action of various boron containing pharmaceuticals [21–23] and determines the structures of boron-based coordination polymers and supramolecular materials [24–27]. Much effort has been devoted to tune the Lewis acidity of boranes, and thus to improve their performance for such applications.

One of the crucial problems in design of new Lewis acids is the quantitative estimation of their strength. Unlike Brønsted acidity, which can be quantitatively assessed accurately using the  $pK_a$  scale, a quantitative measurement of the strength of Lewis acids is a much more dubious undertaking and no universal criterion exists. Whereas the Brønsted acid–base interactions always involve proton transfer allowing a meaningful quantitative comparison, in the Lewis acid–base interactions, involving Lewis acids with widely different electronic and steric substituents, there is no such common denominator. Therefore, quantitative determination of Lewis acid strength to create the Lewis acidity scale similar to the  $pK_a$  scale for Brønsted acidity is extremely difficult and challenging.

Since Lewis first proposed his acid–base theory in 1923, many attempts have been made to quantify Lewis acidity, for example, by correlating Lewis acid strength with thermodynamic data (such as the Lewis acid – Lewis base adduct formation enthalpy), chemical

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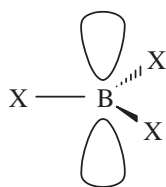


Chart 1.

reactivity, or spectroscopic data, etc. [28,29]. Regardless of the approach used to predict the relative strengths of Lewis acids, it is assumed that a stronger coordinate covalent bond is due to the increased Lewis acidity when the Lewis base is held constant. However, it has to be borne in mind that relative Lewis acidity can vary widely against different Lewis bases. For example,  $\text{BH}_3$  forms more stable adducts with thioethers than  $\text{BF}_3$ , whereas for ethers the reverse is true [30]. Similarly, the Lewis acidity for  $\text{BCl}_3$  with respect to strong bases, such as  $\text{NH}_3$ , is higher than for  $\text{BF}_3$ , whereas toward weak bases, such as  $\text{CO}$ ,  $\text{BF}_3$  is a stronger acid than  $\text{BCl}_3$  [31]. In general, these apparent contradictions can be explained by Pearson's hard and soft acids and bases (HSAB) principle [32–34]. According to Pearson's HSAB principle, hard acids prefer to bind to hard bases while soft acids prefer to bind to soft bases. Hard acids are characterized by small acceptor atoms that have outer electrons not easily excited and that bear considerable positive charge. Soft acids have acceptor atoms with lower positive charge, large size, and easily excited outer electrons. This principle has

been proved to be useful in rationalizing and classifying a large number of chemical reactions involving Lewis acid–base interactions in a qualitative manner, but it gives no basis for a quantitative treatment.

Another important example that can be found in many textbooks is the relative Lewis acidity of boron trihalides. Here, the stability of the  $\text{X}_3\text{B}\cdot\text{NH}_3$  complexes increases in the order  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$ , that is contrary to that expected from the electronegativity scale, which suggests that boron trifluoride should be the stronger Lewis acid in the series owing to more efficient removal of electron density from the boron centre with the highly electronegative fluorine atoms [35]. A very simple explanation for this trend is that the charge donation from fluorine lone pairs into the empty p-orbital on boron is more efficient than the charge donation of chlorine, bromine and iodine lone pairs owing to poorer overlap of these larger p-orbitals with the small p-orbital of boron. However, modern calculations of boron Lewis acidity demonstrate that the coordinate covalent bond strengths are not an adequate measure of Lewis acidity. Rather, Lewis acidity should be gauged by the ability of boron to accept an electron pair (electron pair affinity) [36] or vertical electron affinity [37]. The examples above demonstrate how complicated the factors governing Lewis acidity of boron compounds can be.

This paper discusses the impact of different factors in determining the Lewis acidity of boron compounds and the development of a Lewis acidity scale based on known NMR spectral data.

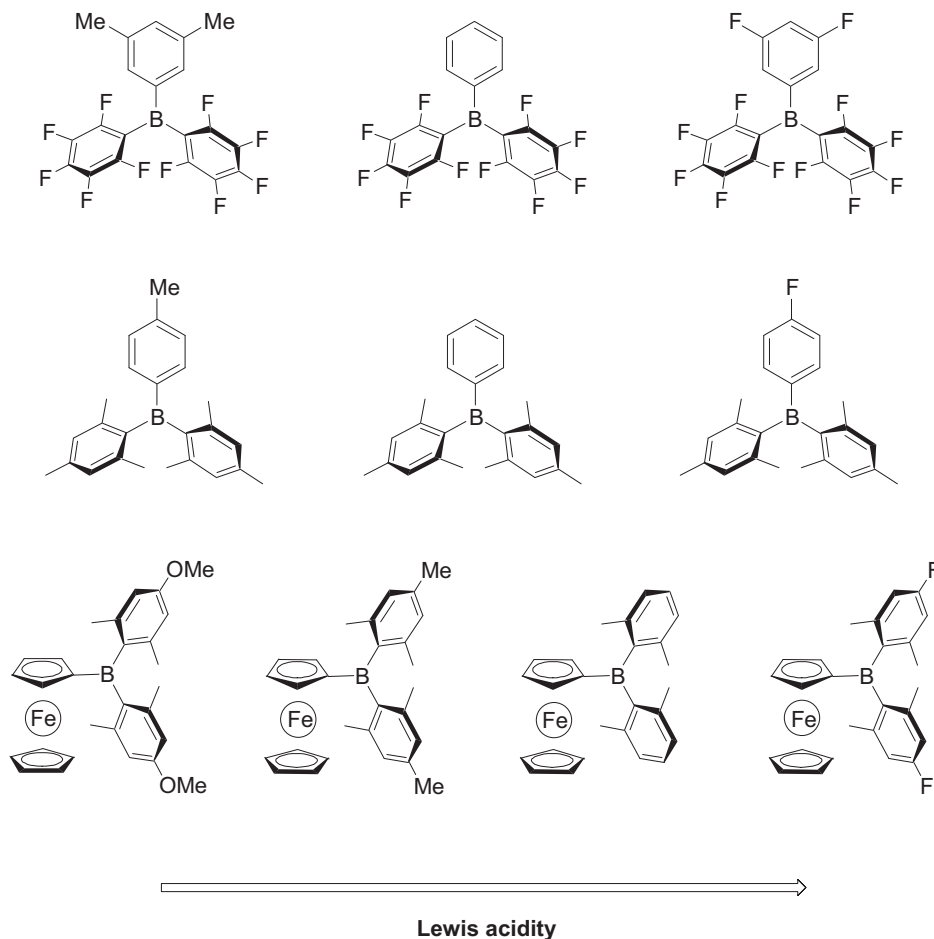


Chart 2.

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