Review Article

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A Short Chronological Review on the Syntheses of Amine-Boranes

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ABSTRACT

Since their discovery by Burg and Schlesinger in 1937, amine-boranes have enjoyed a rich preparative history and have experienced reinvigorated interest as valuable compounds. These borane complexes have been implemented in a variety of applications, spanning from reagents in organic syntheses to hydrogen storage materials. The importance of amine-boranes derives especially from their reductive abilities. Given the utility of amine-boranes and their current resurgence, a mini review on their general properties and notable preparations is both timely and potentially of interest to organic and materials chemists alike.

1. Introduction

Formally, amine-boranes can be described as complexes of borane, which acts as a Lewis acid, and an amine, which acts as a Lewis base. In this complex, the nitrogen atom's lone pair of electrons forms a coordinate covalent, also known as a dative, bond via donation into the vacant borane 2*p* orbital (Figure 1). [1] Such borane adducts can typically be formed with any Lewis base (molecules containing nitrogen, oxygen, phosphorous, or sulfur, wherein the hetero-atom possesses an available pair of non-bonding electrons). Common, simplistic examples of these classical adducts include ammonia-borane (NH_3-BH_3, AB), borane-tetrahydrofuran (BH_3-THF, BTHF), phosphine-borane (PH_3-BH_3, PB), borane-dimethylsulfide [BH_3-$S(CH_3)_2$, BDMS, DMSB], etc.

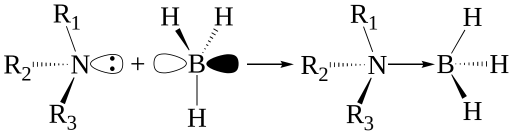

Figure 1. sp3**σ**-p**σ** dative bond formation in an amine-borane

The discovery of a boron-nitrogen dative bond is attributable to Gay-Lussac in 1809 [2], and in 1937, Burg and Schlesinger were credited with the first report of an amine-borane, trimethylamine-borane (Figure 2). [3] With regards to Gay-Lussac, Burg, and Schlesinger, their initial discoveries have ushered more than three-quarters of a century (and beyond) of research into amine-boranes and their derivatives, with diverse applications ranging from reagents in organic syntheses [4] to hydrogen storage materials [5] to pharmacologically active compounds. [6]

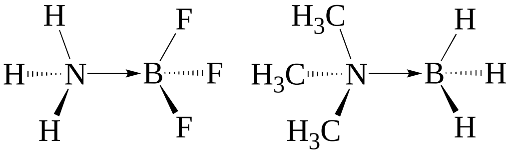

Figure 2. Ammonia-trifluoroborane (left) & trimethylamine-borane (right)

The first historical application of amine-boranes is taken to be as reducing agents, as noted in Hutchins et al.'s seminal 1984 review. [7] A full treatment of the numerous applications of amine-boranes and their derivatives, as well as their relatives like phosphine- (or phosphane-) and sulfide-boranes, is not within the scope of this introduction, though such literature serves as the basis for several fine investigations [6c, 8] and reviews (Figure 3 [9]). [1, 2b, 7, 10].

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