

Review

# Recent developments in the chemistry of 1,3,2-diazaborolines-(2,3-dihydro-1*H*-1,3,2-diazaboroles)

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Received 6 October 2006; accepted 19 February 2007

Available online 25 February 2007

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## Abstract

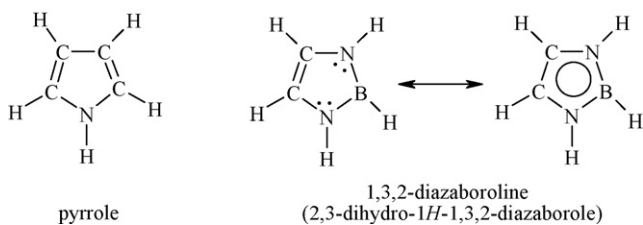
1,3,2-Diazaborolines (2,3-dihydro-1*H*-1,3,2-diazaboroles) are compounds at the interface between inorganic, organometallic and organic chemistry. The planar rings with 6 $\pi$ -electrons may be regarded as heteroarenes, as evident by NMR and photoelectron spectra and confirmed by quantum chemical studies. High-yield syntheses of functionalized 1,3,2-diazaborolines have been elaborated, providing a prolific area of chemistry. Conjugation of the vacant 2p<sub>z</sub>-orbital on the boron center with the  $\pi^*$  orbital of attached organic  $\pi$ -systems proved to be responsible for unique absorption and emission characteristics of 1,3,2-diazaborolinyl functionalized biphenyls, thiophenes and dithiophenes. Most of the functionalized diazaborolines show clean irreversible oxidation waves in their cyclovoltammograms.

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**Keywords:** Diazaborolines; Heteroarenes; Luminescence; Structures

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Scheme 1. Isoelectronic systems; pyrrole and 1,3,2-diazaboroline.

## 1. Introduction

Heterocycles containing boron and nitrogen atoms play an important and fascinating role in main group chemistry. The concept of isoelectronic and isosteric compounds was successfully applied to carbon–carbon and boron–nitrogen containing molecules [1]. Thus, the replacement of a C=C unit in pyrrole affords 2,3-dihydro-1*H*-1,3,2-diazaboroles, which were formerly addressed as 1,3,2-diazaborolines. As in a first review article on these compounds published in 2001 for the sake of clarity and readability the latter nomenclature is also preferred in this account (Scheme 1) [2].

Since the first report on a representative of this class by Merriam and Niedenzu, who catalytically dehydrogenated the corresponding fully saturated diazaborolidine (Scheme 2) [3] and an alternative protocol elaborated by Weber and Schmid who utilized the sodium amalgam reduction of diazaborolium salts (Scheme 2) the chemistry of 1,3,2-diazaborolines developed continuously [4].

A series of 1,3,2-diazaborolines with alkyl- and aryl-substituents at the heteroatoms were synthesized, and their molecular and electronic structures were carefully studied [5–7]. Up to the middle of the 1990s comparatively little work on the chemistry of such rings was accomplished. Reports on  $\pi$ -complexation to the [Cr(CO)<sub>3</sub>] fragment [7–9] as well as N–Si

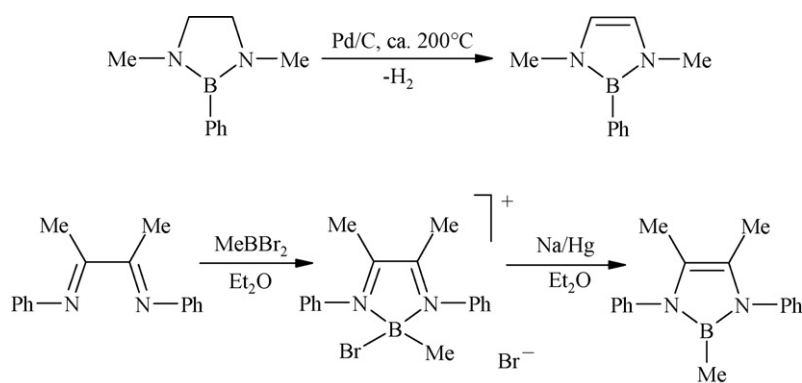
cleavage by alkali amides and alkoxides [7,10] provided some insight into the synthetic potential of these interesting molecules. This situation changed considerably when high-yield syntheses of 1,3,2-diazaborolines with halide substituents at the boron atom were devised [11,12]. This target was reached either by a protocol according to Scheme 2 via the pregenerated 1,3,2-diazaborolium salts or by reacting a 1,4-diazabutadiene with lithium metal prior to the cyclocondensation with boron trihalides (Scheme 3).

Halide replacement by hydride, carbon-, nitrogen-, and tin-nucleophiles now became feasible [12–14]. Whereas the previous review provided an overview of 1,3,2-diazaborolines with particular emphasis placed on synthetic and structural aspects, this report highlights the remarkable richness of their chemistry with respect to the physico-chemical properties and their potential use as organic materials in optoelectronic devices. This account covers the literature of the years 2001–2006.

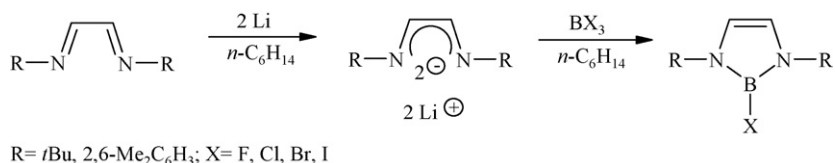
## 2. Synthesis of 1,3,2-diazaborolines

To date there are mainly three different methods for the construction of the ring skeleton of the title compounds: (a) the catalytic dehydrogenation of diazaborolidines; (b) the alkali-metal reduction of 2-halo-1,3,2-diazaborolium salts; and (c) the cyclocondensation of boron halides with dilithiated 1,4-diazabutadienes (Schemes 2 and 3). For several good reasons it is appropriate to also include benzo-1,3,2-diazaborolines in this review. They are readily available by the base-assisted cyclocondensation of 1,2-phenylenediamines with organoboron dihalides and/or boron trihalides (Scheme 4).

Of course halide replacement reactions by suitable nucleophiles in the sense of peripheral reactions remain an important approach to a broad variety of functionalized 1,3,2-diazaborolines (Scheme 5).



Scheme 2. Synthetic approaches to the first 1,3,2-diazaborolines.



Scheme 3. Synthesis of 1,3,2-diazaboroles via dilithiated 1,4-diazabutadiene.

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