

# Synthetic, Cyclovoltammetric, and UV-Photoelectron Spectroscopic Studies of 2,3-Dihydro-1*H*-1,3,2-diazaboroles and 1,3,2-Diazaborolidines

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The oxidation potentials  $E_{\text{ox}}$  of a series of 2,3-dihydro-1*H*-1,3,2-diazaboroles  $\text{t}^{\text{Bu}}\text{NCH}=\text{CHN}(\text{t}^{\text{Bu}})\text{BR}$  (**1a–i**) and of the corresponding saturated 1,3,2-diazaborolidines **2a** (R = NH<sub>2</sub>), **2b** (OMe), **2c** (Me), **2d** (NMe<sub>2</sub>), **2e** (H), **2f** (SMe), **2g** (SnMe<sub>3</sub>), **2h** (Br), **2i** (CN) were determined by cyclovoltammetry in CH<sub>2</sub>Cl<sub>2</sub> solution. The potentials  $E_{\text{ox}}$  of the irreversible electrochemical oxidations range from  $E_{\text{ox}} = -288$  mV (**1a**) to 752 mV (**1i**). In contrast to this,  $E_{\text{ox}}$  of the corresponding diazaborolidines are anodically shifted by 260 mV (**1d**, **2d**) to 752 mV (**1b**, **2b**) and vary from 280 mV (**2a**) to 1164 mV (**2i**). Gas-phase photoelectron spectra of representatives of both series of compounds were recorded and assessed by density functional calculations. The first ionization potentials of the 2,3-dihydro-1*H*-1,3,2-diazaboroles range in the series **1c** (7.1 eV) < **1f** (7.3 eV) < **1e** = **1h** (7.4 eV) < **1i** (7.7 eV). They differ by less than 0.3 eV from the first ionization potentials determined for the saturated analogues [1st IP for **2c** (7.3 eV) < **2e** = **2f** (7.4 eV) < **2h** (7.7 eV)].

## Introduction

The recent development of high-yield syntheses of boron-functionalized 2,3-dihydro-1*H*-1,3,2-diazaboroles (**I**)<sup>1</sup> has given a new impact upon the chemistry of such compounds. Chemical reactions proceed either with retention of the ring skeleton, e.g., nucleophilic displacement processes at the boron center,<sup>2</sup> or with ring transformations, as given in the reaction with diphenylketene to afford 1,3,2-oxazaborolidines.<sup>3</sup> With regard to the prolific chemistry of N-heterocyclic carbenes (Arduengo-carbenes) (**II**)<sup>4</sup> and their silicon and germa-

nium analogues **III**<sup>5</sup> and **IV**<sup>6</sup> the quest for analogous boron species of type **V** was intriguing. Whereas all our initial attempts for the generation of salts containing anions such as **V** by the reduction of appropriate precursors remained fruitless,<sup>7</sup> analogous gallanides **VI** are possible.<sup>8</sup>

In contrast to acyclic amino(halogeno)boranes, where alkali metal reduction has led to diborane (4) derivatives (Me<sub>2</sub>N)(R)B–B(R)(NMe<sub>2</sub>),<sup>9</sup> monoanions [(Me<sub>2</sub>N)(R)B–B(R)(NMe<sub>2</sub>)]<sup>–</sup>,<sup>10</sup> and dianions [(Me<sub>2</sub>N)(R)B–B(R)(NMe<sub>2</sub>)]<sup>2–</sup>,<sup>11</sup> all our attempts to chemically reduce **1f** or **1h** did not furnish the expected diborane **VII**.<sup>7</sup>

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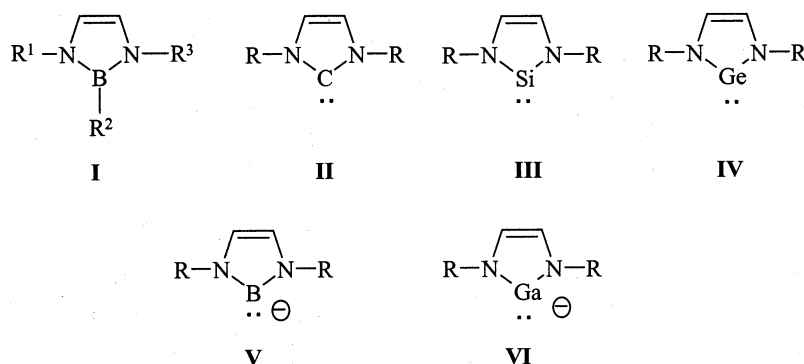
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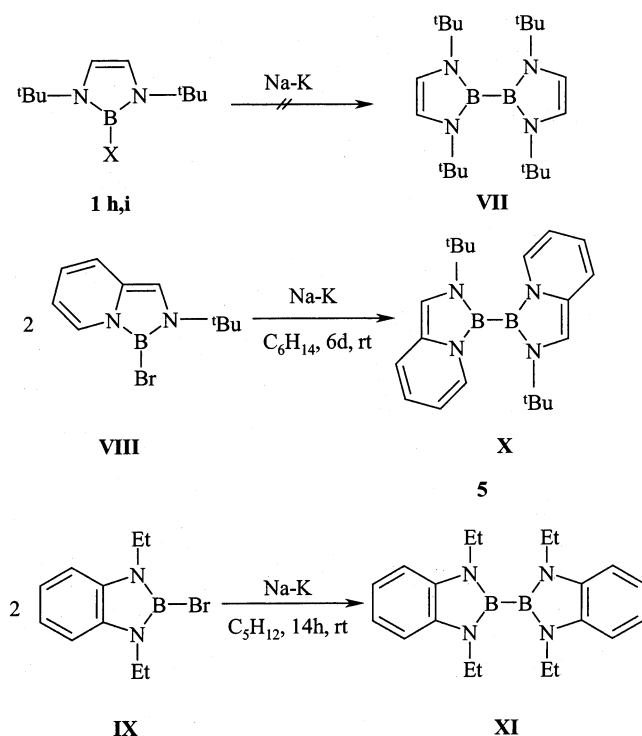
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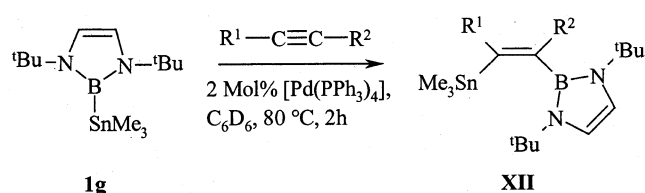
## Scheme 1



## Scheme 2



## Scheme 3



stereoselective formation of alkenes **XII**, as a result of the insertion of the alkynes into the Sn–B bond<sup>14</sup> (Scheme 3)

In a catalyzed reaction an alkyne is inserted in the boron–boron bond of **XIII** to yield bis-(boryl)alkenes **XIV**<sup>15</sup> (Scheme 4).

Another interesting oxidation is the cleavage of the Si–B-bond of the tricyclohexylphosphine(trimethylsilyl)-borane adduct **XV**<sup>16</sup> by iodine (Scheme 5). At this point, it seems necessary to study the redox chemistry of our 2,3-dihydro-1*H*-1,3,2-diazaboroles in more detail. We decided to perform cyclovoltammetric studies to obtain reliable information on the redox behavior of these heterocycles. To correlate the results, obtained in solution, with their behavior in the gas phase, He I photoelectron spectra were recorded and corroborated by density functional calculations of the ionization potentials ( $I_p$ ) of **1c**, **1e**, **1f**, **1h**, **1i**, and the 1,3,2-diazaborolidines as their saturated counterparts.

## Results and Discussion

The 1,3,2-diazaboroles **1a–g,i** employed in this study were conveniently obtained from 2-bromo-2,3-dihydro-1*H*-1,3,2-diazaborole **1h** by nucleophilic displacements as previously described in the literature<sup>1–3</sup> (Scheme 6).

Diazaborolidine **2h** results from the reaction of Et<sub>3</sub>N–BBr<sub>3</sub> with *N,N'*-di-*tert*-butylethylenediamine in the presence of 1 equiv of triethylamine in boiling hexane. The product was isolated as a colorless microcrystalline solid in 84% yield. Compounds **2a–d,f,g,i** were available from **2h** by treatment with a suitable nucleophile. Aside from solid **2i** all other compounds were obtained as colorless to pale yellow oils in modest

However, with 1,3,2-diazaboroles where the five-membered heterocycle is fused to an aromatic ring as given in **VIII**<sup>12</sup> and **IX**,<sup>13</sup> clean conversion into the diboranes **X** and **XI** was effected by treatment with a Na–K alloy (Scheme 2).

On the other hand, it is well known that certain boron-containing species serve as reducing agents. However in most cases, e.g., B<sub>2</sub>H<sub>6</sub>, the boron atom maintains its formal oxidation number (+3) and only the substituent is involved in the electron transfer. There exists a few examples where during an oxidation process the oxidation number of the boron atom is also increased. Thus, the reaction of compound **1g** with an equimolar amount of alkynes in the presence of a catalytic amount of [Pd(PPh<sub>3</sub>)<sub>4</sub>] led to the regio- and

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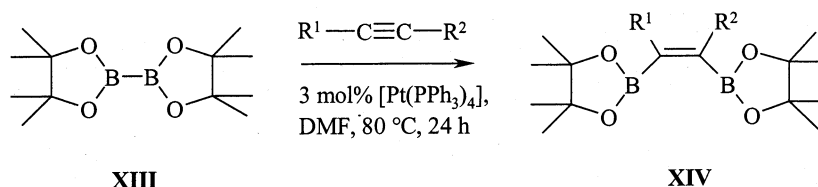
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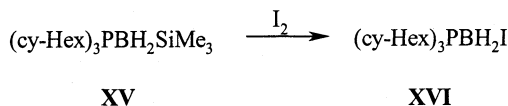
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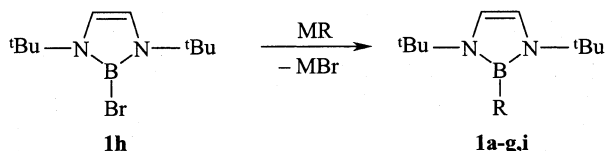
## Scheme 4



## Scheme 5

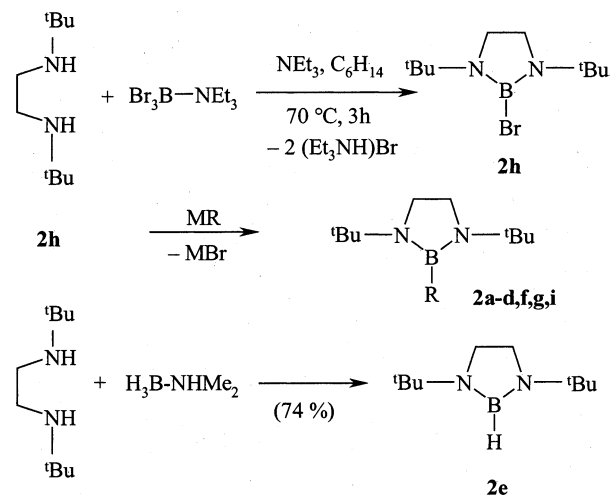


## Scheme 6



| 1 | a               | b   | c  | d                | e                  | f   | g                 | i  |
|---|-----------------|-----|----|------------------|--------------------|-----|-------------------|----|
| R | NH <sub>2</sub> | OMe | Me | NMe <sub>2</sub> | H                  | SMe | SnMe <sub>3</sub> | CN |
| M | H               | Na  | Li | H                | LiAlH <sub>3</sub> | Na  | Li                | Ag |

## Scheme 7



| 2       | a               | b   | c  | d                | f   | g                 | i  |
|---------|-----------------|-----|----|------------------|-----|-------------------|----|
| R       | NH <sub>2</sub> | OMe | Me | NMe <sub>2</sub> | SMe | SnMe <sub>3</sub> | CN |
| M       | H               | Na  | Li | H                | Na  | Li                | Ag |
| yield % | 91              | 86  | 91 | 89               | 83  | 36                | 96 |

(2g) (36%) to excellent yields (83–96%). In contrast to this, compound 2e (R = H) was synthesized as a colorless oil in 74% yield from equimolar amounts of *N,N'*-di-*tert*-butylethylenediamine and H<sub>3</sub>B-NHMe<sub>2</sub> (Scheme 7).

Inspection of the <sup>11</sup>B{<sup>1</sup>H} NMR spectra of the novel 1,3,2-diazaborolidines 2a–i showed an increased shielding as follows: 2c [δ 33.2; Δδ (2c – 1c) = 7.0] > 2f [31.6; 8.3] > 2d [28.0; 5.2] > 2g [27.3; 1.5]; > 2e [26.4; 7.5] > 2a [25.7; 3.6] > 2h [24.7; 8.5] > 2i [18.9; 6.9]. These resonances appear markedly deshielded relative to the <sup>11</sup>B NMR signals of the corresponding 1,3,2-diazaboroles 1a–i (Δδ = 1.5–8.5). The increased shielding of the unsaturated (6 π electrons) heterocycles

Table 1. Oxidation Potentials of 1a–i in CH<sub>2</sub>Cl<sub>2</sub> vs Fc/Fc<sup>+</sup>

|                     | 1a              | 1b  | 1c  | 1d               | 1e  | 1f  | 1g                | 1h  | 1i  |
|---------------------|-----------------|-----|-----|------------------|-----|-----|-------------------|-----|-----|
| R                   | NH <sub>2</sub> | OMe | Me  | NMe <sub>2</sub> | H   | SMe | SnMe <sub>3</sub> | Br  | CN  |
| E <sub>ox</sub> /mV | –288            | –58 | 124 | 158              | 310 | 354 | 396               | 576 | 752 |

Table 2. Oxidation Potentials of 2a–i in CH<sub>2</sub>Cl<sub>2</sub> vs Fc/Fc<sup>+</sup>

|                     | 2a              | 2b  | 2c  | 2d               | 2e  | 2f  | 2g                | 2h  | 2i   |
|---------------------|-----------------|-----|-----|------------------|-----|-----|-------------------|-----|------|
| R                   | NH <sub>2</sub> | OMe | Me  | NMe <sub>2</sub> | H   | SMe | SnMe <sub>3</sub> | Br  | CN   |
| E <sub>ox</sub> /mV | 280             | 516 | 592 | 418              | 662 | 790 | 754               | 993 | 1164 |

agrees with some cyclic 6π-electron delocalization within the planar rings.

**Electrochemical Studies.** First, it was of interest to find out whether the unsaturated heterocycles can be reduced electrochemically to give the desired boranide anion.

The cyclovoltammograms of the diazaboroles 1h (R = Br) and 1i (R = CN) look very similar. Most importantly no reductive peak was observed. Obviously more negative voltages are required. This unusual stability toward reduction could stem from their aromatic (6 π electrons) stabilization.

The cyclovoltammograms of all the unsaturated compounds 1a–i show a significant oxidation signal. With scan rates from 5 to 700 mV s<sup>–1</sup> no reversibility or quasireversibility was observed. In addition to the experiment at 298 K the oxidation of compound 1e was repeated at 258 K. At this temperature, the oxidation potential of the hydroborole is anodically shifted by 113 mV. Again, no quasireversibility was observed, which points to the rapid decomposition of the oxidized species in solution or at the surface of the electrode. The oxidation potentials were confirmed by square-wave voltammetry. The potentials of the 1,3,2-diazaboroles were summarized in Table 1 (vs Fc/Fc<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> at 298 K).

The oxidation potentials vary strongly with the substituents at the boron atom. These trends can be rationalized by the donor/acceptor qualities of the respective substituent. Thus, the amino group as well as the methoxy group function essentially as π-donors toward the boron–nitrogen heterocycle, whereas bromide and cyanide have to be considered as acceptors. Keeping with this, the observed potentials vary from E<sub>ox</sub> = –288 mV (for 1a; R = NH<sub>2</sub>) to E<sub>ox</sub> = 752 mV (for 1i; R = CN). The potentials are anodically shifted in the order 1a (–288 mV) < 1b (–58 mV) < 1c (124 mV) < 1d (158 mV) < 1e (310 mV) < 1f (354 mV) < 1g (396 mV) < 1h (576 mV) < 1i (752 mV). For comparison we also investigated the electrochemical oxidation of the saturated diazaborolidines 2 with an identical substitution pattern. The oxidation potentials, taken from square-wave experiments, are given in Table 2 (vs Fc/Fc<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> at 298 K).

**Table 3. Differences  $\Delta E_{\text{ox}}$  in the Oxidation Potentials of Compounds 1a–i and 2a–i in mV**

|  | 1,2a            | 1,2b | 1,2c | 1,2d             | 1,2e | 1,2f | 1,2g              | 1,2h | 1,2i |
|--|-----------------|------|------|------------------|------|------|-------------------|------|------|
| R  | NH <sub>2</sub> | OMe  | Me   | NMe <sub>2</sub> | H    | SMe  | SnMe <sub>3</sub> | Br   | CN   |
| $\Delta E_{\text{ox}} = E_{\text{ox},2} - E_{\text{ox},1}$ | 548             | 566  | 468  | 260              | 360  | 436  | 358               | 400  | 412  |

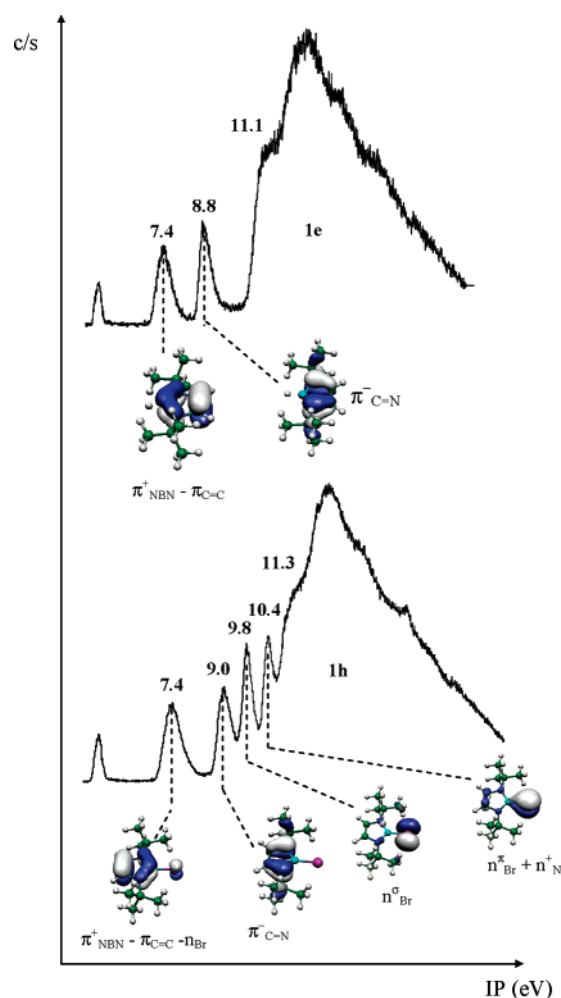
An situation analogous to that with compounds **1a–i** was encountered. The oxidation process is irreversible and the potentials vary in the same way depending on the substituents at the boron center. The compounds are less easily oxidized within the series **2a** (280 mV) < **2d** (418 mV) < **2b** (516 mV) < **2c** (592 mV) < **2e** (662 mV) < **2g** (754 mV) < **2f** (790 mV) < **2h** (993 mV) < **2i** (1164 mV). The influences of the substituents of the 1,3,2-diazaboroles and 1,3,2-diazaborolidines are comparable and follow the same trend. It is obvious that the potentials of **2** are anodically shifted by 260 to 566 mV. The differences are compiled in Table 3. This observation may be rationalized by the fact that the nature of the HOMO is different in **1** and **2**. The ease of the oxidation of the NH<sub>2</sub> derivatives **1a** and **2a** in comparison to the NMe<sub>2</sub> derivatives **1d** and **2d** is surprising and might be rationalized by a facile oxidation of the amino substituent with release of H<sup>+</sup> ions. This is, of course, not possible with **1d** and **2d**.

**UV-Photoelectron Spectra and Theoretical Studies.** He I PE spectra of selected diazaboroles (**1c**, **1e**, **1f**, **1h**, **1i**) and diazaborolidines (**2c**, **2e**, **2f**, **2h**) have been recorded in order to determine their electronic properties and estimate the effect of substitution on the boron atom on the energetic position of the different MOs. As this is effected in the gas phase, complications by solvation or by decomposition at the surface of the electrode are absent. The PE spectra of **1e**, **1h**, **2e**, and **2h** are presented in Figures 1 and 2, and the ionization potentials of all studied compounds are reported in Table 5.

The PE spectrum of **1e** (Figure 1) presents two first bands at 7.4 and 8.8 eV and a broad peak with a shoulder at 11.1 eV. The PE spectrum of its saturated analogue **2e** (Figure 2) displays two first bands at 7.4 and 9.4 eV and the corresponding shoulders at 10.6 and 11.5 eV. For **1h** (Figure 1), four first bands at 7.4, 9.0, 9.8, and 10.4 eV are clearly distinguished, whereas the PE spectrum of **2h** (Figure 2) presents three first ionizations at 7.7, 9.2, and 9.8 eV.

To assign these different PE bands, density functional theory calculations have been carried out on selected diazaboroles and diazaborolidines at the B3LYP/6-311(d,p) level of theory.

The geometrical parameters of diazaboroles **1c**, **e**, **f**, **h**, **i** and diazaborolidines **2c**, **e**, **f**, **h**, **i** are summarized in Table 4. As expected, for **1** the five-membered diazaborole ring is planar ( $\Sigma\text{B}$ : 360°,  $\Sigma\text{N}_1$ : 360°,  $\Sigma\text{N}_2$ : 360°). The saturated heterocycle **2** is slightly twisted (C1N1BN2:  $\Phi_{2e}$ : 7.5°,  $\Phi_{2c}$ : 9.2°,  $\Phi_{2h}$ : 9.3°,  $\Phi_{2i}$ : 9.2°,  $\Phi_{2f}$ : 0.5°) with a planar boron atom and two nearly sp<sup>2</sup>-hybridized nitrogen atoms. The BN bond lengths in **2** (1.424–1.446 Å) are slightly shorter than those of the corresponding unsaturated compounds **1** (1.436–1.458 Å). The endocyclic NC bond lengths in diazaborolidines **2** (1.469–1.474 Å) are longer than in the corresponding diazaboroles **1** (1.395–1.403 Å). The endocyclic carbon–carbon bond lengths are in the range of a double bond for **1** and a single bond for **2**.

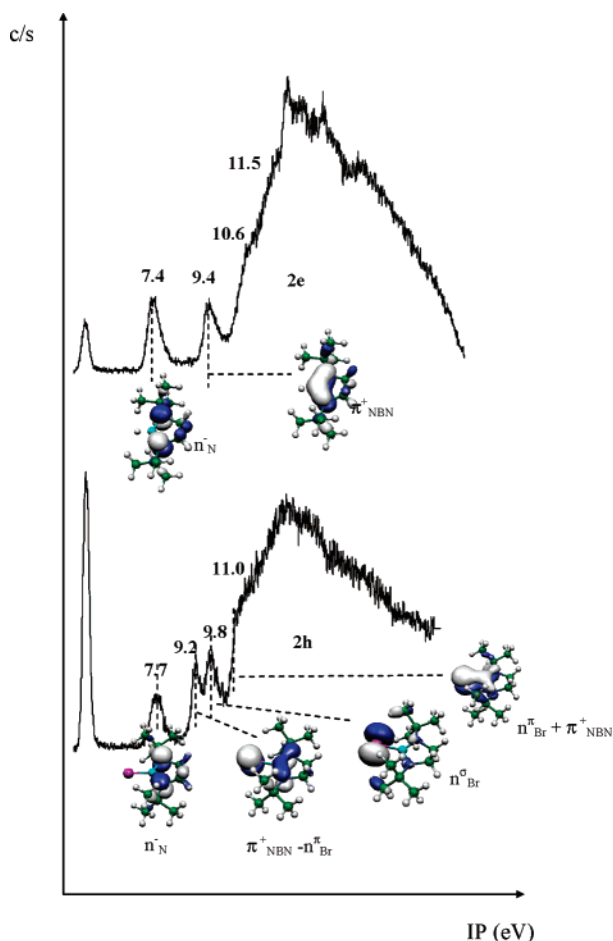
**Figure 1.** He I PE spectra of **1e** and **1h**.

All these calculated geometrical parameters are in quite good agreement with X-ray structural data of diazaboroles and diazaborolidines.<sup>2,17,18</sup> Thus, the endocyclic bond lengths determined for **1g**<sup>2b</sup> [B–N 1.439(7) Å, C–N 1.379(7) Å, C–C 1.344(8) Å] fall in the range calculated for diazaboroles. The endocyclic angles in **1g** [B–N–B 105.0(4)°; B–N–C 107.1(4)°, 108.1(4)°; N–C–C 109.7(5)°, 110.2(5)°] are also consistent with the computational results. The experimental as well as the theoretical data agree with a significant delocalization of the nitrogen lone pairs and  $\pi$  electrons of the carbon–carbon double bond into the vacant 2p<sub>z</sub> orbital of the boron atom in **1**.

To assign different ionizations in all PE spectra, the energetic position of the Kohn–Sham orbitals ( $\epsilon_{\text{KS}}$ ) and the “corrected” (see theoretical section) and TD-DFT calculated ionization potentials have been determined. All these IP estimations are based on geometries obtained with B3LYP/6-311G(d,p) and are displayed in Tables 5 and 6.

For **1**, the first ionization potential corresponds mainly to the bonding combination of the nitrogen lone pairs ( $n^+_{\text{N}^7}$ ) delocalized in the p boron vacant orbital ( $\pi^+_{\text{NBN}}$ ) in antibonding interaction with the  $\pi_{\text{C=C}}$  orbital. The nature of the second ionization potential (third one for **1f**) fits with the  $\pi^-_{\text{C=N}}$  orbital which is due to the antibonding nitrogen lone pairs combination in interaction with the  $\pi^*_{\text{C=C}}$  orbital (for **1f** the second IP corresponds to the ionization of the  $\sigma$  sulfur lone pair).





**Figure 2.** He I PE spectra of **2e** and **2h**.

The lowest value of IP is obtained for the methyl-substituted diazaborole **1c**; the highest ones are observed for the cyano derivative **1i** and the bromo derivative **2h**. For diazaborolidines **2**, the natures of the HOMO and the HOMO-1 are different when compared to their unsaturated analogues. The HOMO corresponds to the nitrogen lone pairs antibonding combination ( $n_{N^{\pi}}$ ), while the HOMO-1 is due to the nitrogen lone pairs bonding combination ( $n_{N^{\sigma}}$ ) (except for **2f**: HOMO-1:  $n_{N^{\sigma}}$  and HOMO-2:  $n_{N^{\pi}}$ ).

The nature and the order of these two highest occupied molecular orbitals are consistent with the CNCD/S calculations of 1,3-dimethyl-2-*tert*-butyl-1,3,2-diazaborole and 1,3-dimethyl-2-*tert*-butyl-1,3,2-diazaborolidine.<sup>19</sup>

The comparison of the experimental ionization potentials and the theoretical results allows us to assign different bands on the PE spectra. We describe here only four PE spectra presented in Figures 1 and 2. For other compounds, the assignments are given in Tables 5 and 6.

The attribution of the first two ionizations for unsaturated diazaboroles should be done as follows: the first band at 7.4 eV for **1e** and **1h** corresponds to the ejection of an electron from the  $n_{N^{\sigma}}$  orbital in interaction with

the  $\pi_{C=C}$  orbital ( $n_{N^{\sigma}} - \pi_{C=C}$  or  $\pi_{NBN}^+ - \pi_{C=C}$ ). The second band of **1e** at 8.8 eV and that of **1h** at 9.1 eV are assigned to the  $n_{N^{\pi}}$  orbital in interaction with the  $\pi_{C=C}^*$  orbital ( $\pi_{C=N}^-$  or  $n_{N^{\pi}} - \pi_{C=C}^*$ ). For **1h**, the following ionizations at 9.8 and 10.4 eV are respectively attributed to the ionization of the  $\sigma$  and  $\pi$  bromine lone pairs ( $n_{Br^{\sigma}}$  and  $n_{Br^{\pi}} + n_{N^{\pi}}$ ). For **2e**, the first ionization potential at 7.4 eV corresponds to the nitrogen antibonding combination of lone pair ( $n_{N^{\pi}}$ ) and the band at 9.4 eV to the nitrogen bonding combination of lone pair ( $n_{N^{\sigma}}$ ). The first ionization potential of **2h** at 7.7 eV is assigned to the removal of an electron from the  $n_{N^{\pi}}$  orbital and the band at 9.2 eV to the ejection of an electron from the  $n_{N^{\sigma}}$  orbital in interaction with the bromine  $\pi$  lone pair ( $n_{N^{\sigma}} - n_{Br^{\pi}}$ ). The following band at 9.8 and the shoulder of the band at 11.0 eV are attributed to the ionization from the  $\sigma$  and  $\pi$  bromine lone pairs ( $n_{Br^{\sigma}}$  and  $n_{Br^{\pi}} + n_{N^{\pi}}$ ), respectively.

We can note that the calculated vertical ionization potentials are very close to the measured photoelectron spectroscopic data of diazaboroles **1**. Larger deviations are observed for **2**, but they do not exceed 0.3 eV. However, for **1c**, **1f**, **2h**, and **2f**, the second TD-DFT ionic states are not correctly correlated with experimental values of IPs. The experimentally observed energetic gaps between the  $n_{N^{\sigma}}$  and  $n_{N^{\pi}}$  orbitals vary from 1.4 to 2 eV [ $\Delta E(n_{N^{\sigma}}/n_{N^{\pi}})$ : 2.0 eV **2e**, 1.7 eV **2c**, 1.5 eV **2h**, 1.9 eV **2f**; 1.4 eV **1e**, 1.8 eV **1c**, 1.7 eV **1h**, 1.5 eV **1i**, 1.7 eV **1f**] (a more important difference is observed for **2e** and **1c**) and correlate fairly well with the theoretically determined energetic gaps [ $\Delta E(n_{N^{\sigma}}/n_{N^{\pi}})$ : 2.01 eV **2e**, 1.66 eV **2c**, 1.34 eV **2h**, 1.85 eV **2f**; 1.62 eV **1e**, 1.69 eV **1c**, 1.73 eV **1h**, 1.50 eV **1i**, 1.64 eV **1f**].

As can be seen from Tables 5 and 6, the substitution effect on the boron atom is not the same for unsaturated and saturated heterocycles **1** and **2**. For **1**, the first and the second IPs seem to be more sensitive to the methyl substitution. Its electron-donating effect lowers significantly these IPs compared to the unsubstituted compound **1e**. A rather strong  $\sigma$  and  $\pi$  electron withdrawing effect is observed for the CN-substituted compound **1i**, for which IP<sub>1</sub> and IP<sub>2</sub> are stabilized (shifted to highest values of IP). Bromine and thiomethyl substitution of diazaboroles led to a slight stabilization of the second IP. The first IP is practically unchanged for **1f** and **1h** when compared to **1e**.

The situation is different for the saturated heterocycles. The first two ionization potentials seem to be more sensitive to the bromine substitution on boron and leads to a stabilization of the  $n_{N^{\sigma}}$  orbital of 0.3 eV compared to the parent compound (R = H) [7.4 eV (**2e**), 7.7 eV (**2h**)]. This fact is consistent with the  $\sigma$ -withdrawing effect of the Br atom. The IP<sub>2</sub>, corresponding to the  $n_{N^{\pi}}$  orbital, is destabilized by 0.2 eV compared to the parent compound [9.4 eV (**2e**), 9.2 eV (**2h**)] and shows that in this case the  $\pi$ -donor effect of the Br atom (destabilizing effect) is more important than its  $\sigma$ -withdrawing effect (stabilizing effect). In the case of **1h**, the  $\pi$ -donor effect of the Br atom is diminished by its  $\sigma$ -attractor effect; therefore the IP is the same for **1e** and **1h**. The methyl substitution (**2c**) gives a more pronounced effect. Indeed, for the second IP we can note 0.4 eV destabilization of the  $n_{N^{\sigma}}$  orbital.

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**Table 4. Geometrical Parameters of Diazaboroles 1 and Diazaborolidines 2**

|                             | <b>1e</b>   | <b>1c</b>   | <b>1i</b>   | <b>1h</b>   | <b>1f</b>   |
|-----------------------------|-------------|-------------|-------------|-------------|-------------|
| Selected Bond Distances (Å) |             |             |             |             |             |
| B–X                         | 1.179       | 1.586       | 1.535       | 1.962       | 1.863       |
| B–N                         | 1.436       | 1.458       | 1.440       | 1.442       | 1.453/1.452 |
| N–C (ring)                  | 1.400       | 1.400       | 1.395       | 1.403       | 1.397/1.398 |
| C–C (ring)                  | 1.352       | 1.344       | 1.351       | 1.344       | 1.346       |
| Selected Bond Angles (deg)  |             |             |             |             |             |
| NBN                         | 106.0       | 104.8       | 106.7       | 107.4       | 105.8       |
| NBX                         | 130.8       | 126.5       | 127.6       | 126.3       | 127.0/127.1 |
| BNC                         | 107.4       | 107.3       | 106.5       | 105.8       | 106.8/106.8 |
| CCN                         | 109.6       | 110.2       | 110.1       | 110.5       | 110.3/110.3 |
| ΣB                          | 360.0       | 360.0       | 360.0       | 360.0       | 360.0       |
| ΣN                          | 360.0       | 360.0       | 360.0/360.0 | 360.0/360.0 | 360.0/360.0 |
|                             | <b>2e</b>   | <b>2c</b>   | <b>2i</b>   | <b>2h</b>   | <b>2f</b>   |
| Selected Bond Distances (Å) |             |             |             |             |             |
| B–X                         | 1.182       | 1.586       | 1.549       | 1.971       | 1.882       |
| B–N                         | 1.424/1.424 | 1.441/1.446 | 1.424/1.424 | 1.427/1.427 | 1.433/1.437 |
| N–C (ring)                  | 1.471/1.472 | 1.469/1.470 | 1.474/1.474 | 1.474/1.474 | 1.470/1.470 |
| C–C (ring)                  | 1.539       | 1.526       | 1.532       | 1.529       | 1.529       |
| Selected Bond Angles (deg)  |             |             |             |             |             |
| NBN                         | 109.8       | 108.6       | 111.5       | 111.9       | 110.0       |
| NBX                         | 125.1/130.5 | 129.3/125.2 | 124.2/124.3 | 124.1/124.1 | 127.0/123.0 |
| BNC                         | 108.2/108.2 | 107.8/107.5 | 106.3/106.4 | 105.7/105.8 | 107.6/107.2 |
| CCN                         | 104.2/104.2 | 103.9/104.1 | 104.2/104.2 | 104.3/104.3 | 105.2/104.3 |
| ΣB                          | 360.0       | 360.0       | 360.0       | 360.0       | 360.0       |
| ΣN                          | 358.6/358.7 | 354.8/356.8 | 355.7/355.9 | 355.6/356.8 | 360.0/359.7 |

**Table 5. Kohn–Sham Energies ( $-\epsilon^{\text{KS}}$ ), “Corrected” IPs, TD-DFT IPs (first IP value:  $\Delta\text{SCF}$ ), and Experimental Ionization Potentials (exptl IP) in eV for the Diazaboroles 1c,e,f,h,i**

| <b>1e</b>  |                         |                |        |          | <b>1c</b>  |                         |                |        |          |
|--|-------------------------|----------------|--------|----------|--|-------------------------|----------------|--------|----------|
| nature of MOs  | $-\epsilon^{\text{KS}}$ | “corrected” IP | TD-DFT | exptl IP | nature of MOs  | $-\epsilon^{\text{KS}}$ | “corrected” IP | TD-DFT | exptl IP |
| $\pi^+_{\text{NBN}} - \pi_{\text{C}=\text{C}}$             | 5.20                    | 7.40           | 7.19   | 7.4      | $\pi^+_{\text{NBN}} - \pi_{\text{C}=\text{C}}$                           | 5.02                    | 7.10           | 6.93   | 7.1      |
| $\pi^-_{\text{C}=\text{N}}$                                | 6.82                    | 9.02           | 8.55   | 8.8      | $\pi^-_{\text{C}=\text{N}}$  | 6.71                    | 8.80           | 8.40   | 8.9      |
| $\sigma_{\text{BN}}, \sigma_{\text{NC}}$                   | 8.80                    | 11.00          | 9.98   | 11.1     | $\sigma_{\text{BN}}, \sigma_{\text{NC}}, \sigma_{\text{CC}^t\text{Bu}}$  | 8.58                    | 10.66          | 9.77   | 10.6     |
| $\sigma_{\text{BH}}, \sigma_{\text{CC}^t\text{Bu}}$        |                         |                |        |          | $\sigma_{\text{BN}}, \sigma_{\text{NC}}, \sigma_{\text{CC}^{\text{Me}}}$ |                         |                |        |          |
| $\sigma_{\text{BN}}, \sigma_{\text{NC}}$                   | 8.83                    | 11.03          | 10.01  | 11.6     | $\sigma_{\text{CC}^t\text{Bu}}$  | 8.83                    | 10.91          | 10.07  | 11.2     |
| <b>1h</b>  |                         |                |        |          | <b>1f</b>  |                         |                |        |          |
| nature of MOs  | $-\epsilon^{\text{KS}}$ | “corrected” IP | TD-DFT | exptl IP | nature of MOs  | $-\epsilon^{\text{KS}}$ | “corrected” IP | TD-DFT | exptl IP |
| $\pi^+_{\text{NBN}} - \pi_{\text{CC}} - \pi^+_{\text{Br}}$ | 5.40                    | 7.40           | 7.26   | 7.4      | $\pi^+_{\text{NBN}} - \pi_{\text{C}=\text{C}}$                           | 5.37                    | 7.40           | 7.20   | 7.3      |
| $\pi^-_{\text{C}=\text{N}}$                                | 7.13                    | 9.13           | 8.76   | 9.0      | $\pi_{\text{S}}^\sigma$  | 5.81                    | 7.74           |        | 8.2      |
| $\pi^\sigma_{\text{Br}}$                                   | 7.32                    | 9.32           | 8.83   | 9.8      | $\pi^-_{\text{C}=\text{N}}$  | 7.01                    | 8.94           |        | 9.0      |
| $\pi^+_{\text{Br}} + \pi^+_{\text{N}}$                     | 7.96                    | 9.96           | 9.76   | 10.4     | $\sigma_{\text{BS}}$   | 8.00                    | 9.93           | /      | 10.2     |
| <b>1i</b>  |                         |                |        |          |  |                         |                |        |          |
| nature of MOs  | $-\epsilon^{\text{KS}}$ | “corrected” IP | TD-DFT | exptl IP |  |                         |                |        |          |
| $\pi^+_{\text{NBN}} - \pi_{\text{CC}} - \pi_{\text{CN}}$   | 5.73                    |                | 7.75   | 7.7      |  |                         |                |        |          |
| $\pi^-_{\text{C}=\text{N}}$                                | 7.38                    |                | 9.35   | 9.3      |  |                         |                |        |          |
| $\pi^-_{\text{CN}}$  | 8.55                    |                | 10.52  | 10.9     |  |                         |                |        |          |
| $\pi_{\text{CN}} + \pi^+_{\text{N}}$                       | 8.96                    |                | 10.93  | 10.33    |  |                         |                |        |          |

## Conclusion and Perspectives

For the studied compounds presented here, we can note for the methyl-cyans and the hydro-substituted 1,3,2-diazaboroles and 1,3,2-diazaborolidines a conspicuous correlation between the CV and PES data (see Figure 3).

In agreement with experimental IPs, **2h** and **1i** are more electron deficient; therefore it is more difficult to oxidize them electrochemically compared to **2e**. Furthermore, **2c** and **1c** are easier to oxidize than the corresponding parent compounds **1e** and **2e**, which is coherent with a lower value of ionization potential.

For the boroles with the bromo and the thiomethyl substituents at the boron atom, the results of the experiments in the gas phase and in solution differ

notably, probably due to kinetic and surface effects.<sup>20</sup> Chemical oxidations and the elucidation of the obtained products are under way.

## Experimental Section

**General Procedures.** All manipulations were performed under an atmosphere of dry dinitrogen or argon using standard Schlenk techniques. All solvents were dried by common methods and freshly distilled prior to use. The compounds  $\text{BuN}^+ \text{CH}=\text{CH}-\text{N}^-(\text{tBu})\text{B}-\text{R}$  (**1a–i**: R =  $\text{NH}_2$ ,<sup>2a</sup> OMe,<sup>7</sup> Me,<sup>21</sup> NMe<sub>2</sub>,<sup>2a</sup> H,<sup>2b</sup> SMe,<sup>7</sup> SnMe<sub>3</sub>,<sup>2b</sup> Br,<sup>2d</sup> CN<sup>2c</sup>) were prepared ac-

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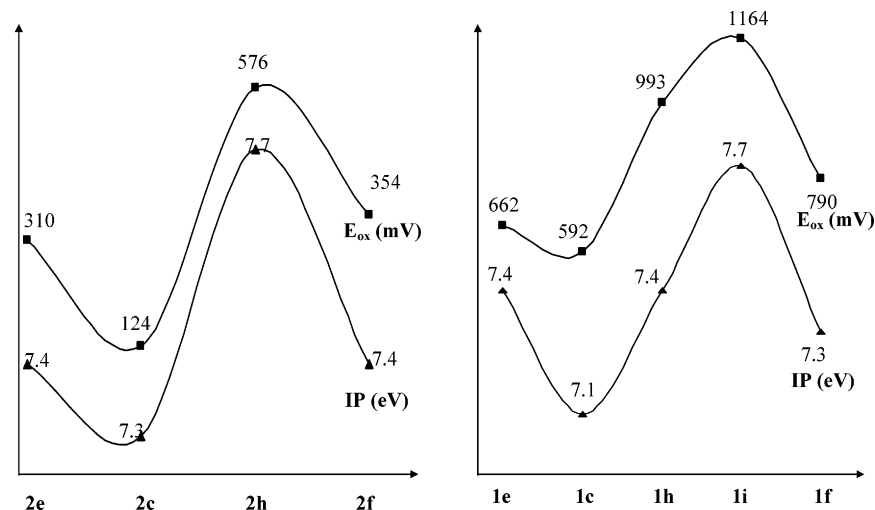


Figure 3. First ionization potential (IP eV) and oxidative peak ( $E_{ox}$  mV) for 1 and 2.

Table 6. Kohn–Sham Energies ( $-\epsilon^{KS}$ ), “Corrected” IPs, TD-DFT IPs (first IP value:  $\Delta$ SCF), and Experimental Ionization Potentials (exptl IP) in eV for the Diazaborolidines 2c,e,f,h

| 2e                             |                  |                |        |              | 2c   |                  |                |        |          |
|--------------------------------|------------------|----------------|--------|--------------|--|------------------|----------------|--------|----------|
| nature of MOs                  | $-\epsilon^{KS}$ | “corrected” IP | TD-DFT | exptl IP     | nature of MOs                                | $-\epsilon^{KS}$ | “corrected” IP | TD-DFT | exptl IP |
| $n^-_N$                        | 5.33             | 7.40           | 7.09   | 7.4          | $n^-_N$                                      | 5.33             | 7.30           | 7.05   | 7.3      |
| $n^+_N$                        | 7.31             | 9.38           | 9.36   | 9.4          | $n^+_N$                                      | 6.99             | 9.00           | 8.96   | 9.0      |
| $\sigma_{BN}, \sigma_{NC}$     | 8.54             | 10.61          | 10.00  | 10.6         | $\sigma_{BN}, \sigma_{NC}, \sigma_{CC^tBu}$  | 8.42             | 10.40          | 9.78   | 10.6     |
| $\sigma_{BH}, \sigma_{CC^tBu}$ |                  |                |        |              | $\sigma_{BN}, \sigma_{NC}, \sigma_{CC^{Me}}$ | 8.58             | 10.50          | 10.00  | 10.6     |
| $\sigma_{BN}, \sigma_{NC}$     | 8.68             | 10.75          | 10.05  | 10.6         | $\sigma_{CC^tBu}$                            |                  |                |        |          |
|                                |                  |                |        |              |  |                  |                |        |          |
| 2h                             |                  |                |        |              | 2f   |                  |                |        |          |
| nature of MOs                  | $-\epsilon^{KS}$ | “corrected” IP | TD-DFT | exptl IP     | nature of MOs                                | $-\epsilon^{KS}$ | “corrected” IP | TD-DFT | exptl IP |
| $n^-_N$                        | 5.75             | 7.70           | 7.47   | 7.7          | $n^-_N$                                      | 5.49             | 7.40           | 7.13   | 7.4      |
| $n^+_N - n^r_{Br}$             | 7.09             | 9.04           | 8.76   | 9.2          | $n^s$  | 5.87             | 7.78           | 7.47   | 8.1      |
| $n^r_{Br}$                     | 7.38             | 9.33           | 8.86   | 9.8          | $n^+_N - n^r_s$                              | 7.34             | 9.25           | 9.08   | 9.3      |
| $n^r_{Br} + n^+_N$             | 8.34             | 10.29          | 10.02  | shoulder11.0 | $\sigma_{BN}, \sigma_{BS}$                   | 8.10             | 10.01          | 9.67   | 10.2     |

ording to literature methods. Boron tribromide,  $H_3BNMe_2H$ ,  $N,N'$ -di-*tert*-butylethylenediamine, trimethyltin chloride, sodium methoxide, sodium thiomethylate, methyl lithium, lithium metal, ammonia, and silver cyanide were purchased from commercial sources.

NMR spectra ( $C_6D_6$ ) were recorded on a Bruker AM Avance DRX 500 spectrometer ( $^1H$ ,  $^{11}B$ ,  $^{13}C$ ) using  $SiMe_4$  and  $BF_3 \cdot OEt_2$  as external standards. UV–vis spectra were recorded on a Perkin-Elmer UV Win Lab spectrometer; mass spectra on a VG Autospec sector field mass spectrometer (Micromass).

The electrochemical experiments were performed with a PAR Model 270A instrument and the relevant software (Model 270). A system of microelectrodes with a three-electrode array was used. As working electrode served a platinum wire (1.5 cm length, 0.5 mm diameter) that was formed as a helix around the counter electrode. A silver wire (1.5 cm length, 1 mm diameter) served as a pseudoreference electrode. All experiments were conducted in a glass device, which was flame-dried prior to use and filled with dry dinitrogen. The determinations were performed in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF) in  $CH_2Cl_2$  and MeCN, with concentrations of the analyte of ca.  $1 \times 10^{-4}$  mol  $L^{-1}$  in the range 0 to 3 V. The cyclic voltammograms were recorded with scan rates of 5–700  $mV s^{-1}$ , whereby the diagrams published here were obtained with a constant scan rate of 100  $mV s^{-1}$ . All published potentials were confirmed by square-wave voltammetry (frequency: 5 Hz). The determination of the oxidation potentials was not possible by cyclic voltammetry alone, because of the irreversibility of the redox process regardless of the scan rate employed. The oxidation

potentials were referenced versus the ferrocene/ferrocinium complex ( $E_{ox} = 0$  eV).

Photoelectron spectra were recorded with a Helectros 0018 spectrometer equipped with a  $127^\circ$  cylindrical analyzer using 21.21 eV He I radiation as a photon source and monitored by a microcomputer supplemented with a digital-to-analogue converter. Helium ionization at 4.98 eV and nitrogen ionizations at 15.59 and 16.98 eV were used for calibration. The spectra contain 2000 points and are accurate to 0.1 eV.

**Theoretical Information.** Calculations were performed with the Gaussian 98<sup>22,23</sup> program package using the density functional theory<sup>24</sup> method. All structures were fully optimized at the B3LYP level.<sup>25a</sup> This functional is built with Becke’s three-parameter exchange functional<sup>25b</sup> and the Lee–Yang–Parr correlation functional.<sup>25c</sup> The 6-311G(d,p) basis set was

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used. The second derivatives were calculated in order to check that the optimized structures are true minima on the potential energy surface. All total energies have been zero-point energy (ZPE) and temperature corrected using unscaled density functional frequencies. Excited states were obtained from density functional theory by its time-dependent development (TD-DFT).<sup>26,27</sup> This calculation is based on the evaluation of the electronic spectrum of the low lying ion, described by the  $\Delta$ SCF corresponding to the first vertical ionization potential,  $IP_v^{cal}$ , calculated as the difference  $E_{cation} - E_{neutral\ molecule}$ . So-called "corrected" IPs were calculated by applying a uniform shift ( $x = |^{-KS}(HOMO) - IP_v^{exp}|$ , where  $^{KS}(HOMO)$  is the highest occupied B3LYP/3-111G(d,g) Kohn–Sham MO energy of the ground-state molecule and  $IP_v^{exp}$  is the lowest energy experimental IP of the molecule, as suggested previously by Stowasser and Hoffmann.<sup>28</sup>

**Preparations.**  **$t$ -BuNCH<sub>2</sub>CH<sub>2</sub>N( $t$ -Bu)BBr (2h).** A solution of boron tribromide (4.35 g, 17.4 mmol) in 10 mL of hexane was slowly added to the chilled solution (0 °C) of triethylamine (3.52 g, 34.8 mmol) in 100 mL of hexane, whereby a white precipitate was formed. After warming to room temperature the solution of *N,N'*-di-*tert*-butylethylenediamine (3.00 g, 17.4 mmol) in 10 mL of hexane was added, and the mixture was heated under reflux for 3 h. Then it was filtered, and the filtrate was evaporated to dryness to afford pure **2h** as a microcrystalline colorless solid, yield 3.81 g (84%) (Found: C, 45.74; H, 8.32; N, 10.57. C<sub>10</sub>H<sub>22</sub>BBR<sub>2</sub> requires: C, 46.02; H, 8.50; N, 10.73). <sup>1</sup>H NMR:  $\delta$  1.28 (s, 18H,  $t$ Bu), 2.91 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  30.3 [s, C(CH<sub>3</sub>)<sub>3</sub>], 41.5 (s, CH<sub>2</sub>), 52.2 [s, C(CH<sub>3</sub>)<sub>3</sub>]. <sup>11</sup>B{<sup>1</sup>H} NMR:  $\delta$  24.7 s. MS/EI (70 eV):  $m/z$  = 261 (M<sup>+</sup>, 12) and 246 (M<sup>+</sup> - CH<sub>3</sub>, 100). CV:  $E_{ox}$  = 976 mV.

**$t$ -BuNCH<sub>2</sub>CH<sub>2</sub>N( $t$ -Bu)BNH<sub>2</sub> (2a).** During 20 min at room temperature gaseous ammonia was bubbled through a hexane solution (60 mL) of compound **2h** (1.02 g, 3.91 mmol). A white precipitate separated from the solution. Thereafter the flask with the reaction mixture was freed from ammonia by a stream of nitrogen for 30 min. Filtration and removal of volatile components in vacuo afforded a clear oil, which was purified by distillation (1 × 10<sup>-3</sup> mbar, 72–75 °C), yield 0.71 g (91%) (Found: C, 63.00; H, 12.78; N, 9.23. C<sub>10</sub>H<sub>24</sub>BN<sub>3</sub> requires: C, 62.62; H, 12.31; N, 10.40). <sup>1</sup>H NMR:  $\delta$  1.17 (s, 18H,  $t$ Bu), 1.86 (s, 2H, NH<sub>2</sub>), 2.99 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  29.9 [s, C(CH<sub>3</sub>)<sub>3</sub>], 44.3 [s, CH<sub>2</sub>], 50.5 [s, C(CH<sub>3</sub>)<sub>3</sub>]. <sup>11</sup>B{<sup>1</sup>H} NMR:  $\delta$  25.7 s. MS/EI (70 eV):  $m/z$  = 197 (M<sup>+</sup>, 12) and 182 (M<sup>+</sup> - CH<sub>3</sub>, 73). CV:  $E_{ox}$  = 280 mV.

**$t$ -BuNCH<sub>2</sub>CH<sub>2</sub>N( $t$ -Bu)BOMe (2b).** Sodium methylate (0.54 g, 9.5 mmol) was dissolved in hexane (50 mL) at 0 °C. The solution of compound **2h** (1.00 g, 3.8 mmol) in hexane (30 mL) was added dropwise, and the resulting mixture was stirred for 1 h at 20 °C. The solvent was removed in vacuo, and the remaining yellow oil was purified by distillation (1 × 10<sup>-3</sup> mbar, 101–104 °C), yield 0.69 g (86%) (Found: C, 61.93; H, 11.70; N, 12.93. C<sub>11</sub>H<sub>25</sub>BN<sub>2</sub>O requires: C, 62.28; H, 11.88; N, 13.21). <sup>1</sup>H NMR:  $\delta$  1.22 (s, 18H,  $t$ Bu), 2.95 (s, 4H, CH<sub>2</sub>), 3.41 (s, 3 H, OCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  29.8 [s, C(CH<sub>3</sub>)<sub>3</sub>], 46.8 [s, CH<sub>2</sub>], 50.5 [s, C(CH<sub>3</sub>)<sub>3</sub>], 53.5 [s, OCH<sub>3</sub>]. <sup>11</sup>B{<sup>1</sup>H} NMR:  $\delta$  26.3 s. MS/EI (70 eV):  $m/z$  = 212 (M<sup>+</sup>, 10), 197 (M<sup>+</sup> - CH<sub>3</sub>, 69). CV:  $E_{ox}$  = 516 mV.

**$t$ -BuNCH<sub>2</sub>CH<sub>2</sub>N( $t$ -Bu)BMe (2c).** A 1.6 M solution of methyl-lithium (2.9 mL, 4.64 mmol) in diethyl ether was diluted with

20 mL of hexane, and the resulting mixture was added dropwise to the chilled hexane solution (40 mL, -10 °C) of compound **2h** (1.00 g, 3.80 mmol). After stirring for 0.5 h at -10 °C it was warmed to room temperature. It was filtered, and the filtrate was freed from solvent and volatile components in vacuo. The oily residue was distilled at 10<sup>-3</sup> mbar to afford product **2c** as a colorless oil (bp 92 °C), yield 68 g (91%) (Found: C, 67.27; H, 12.66; N, 14.08. C<sub>11</sub>H<sub>25</sub>BN<sub>2</sub> requires: C, 67.36; H, 12.85; N, 14.28). <sup>1</sup>H NMR:  $\delta$  0.60 (s, 3H, BCH<sub>3</sub>), 1.20 (s, 18H,  $t$ Bu), 3.03 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  30.7 [s, C(CH<sub>3</sub>)<sub>3</sub>], 45.3 (s, CH<sub>2</sub>), 51.1 [s, C(CH<sub>3</sub>)<sub>3</sub>]. <sup>11</sup>B{<sup>1</sup>H} NMR:  $\delta$  33.2 s. MS/EI (70 eV):  $m/z$  = 196 (M<sup>+</sup>, 33) and 181 (M<sup>+</sup> - CH<sub>3</sub>, 27). CV:  $E_{ox}$  = 592 mV.

**$t$ -BuNCH<sub>2</sub>CH<sub>2</sub>N( $t$ -Bu)BNMe<sub>2</sub> (2d).** At room temperature a stream of gaseous dimethylamine was bubbled through a hexane solution (50 mL) of compound **2h**, whereby a white precipitate was formed. Excess of amine was removed by a stream of nitrogen during 30 min. It was filtered, and the filtrate was evaporated to dryness to afford pure product **2d** as a pale yellow oil, yield 1.92 g (89%) (Found: C, 63.67; H, 12.26; N, 18.08. C<sub>12</sub>H<sub>26</sub>BN<sub>3</sub> requires: C, 64.01; H, 12.53; N, 18.66). <sup>1</sup>H NMR:  $\delta$  1.18 (s, 18H,  $t$ Bu), 2.33 (s, 6H, NCH<sub>3</sub>), 3.00 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  30.0 [s, C(CH<sub>3</sub>)<sub>3</sub>], 39.8 (s, NCH<sub>3</sub>), 43.3 (s, CH<sub>2</sub>), 50.6 [s, C(CH<sub>3</sub>)<sub>3</sub>]. <sup>11</sup>B{<sup>1</sup>H} NMR:  $\delta$  28.0 s. MS/EI (70 eV):  $m/z$  = 225 (M<sup>+</sup>, 14), 210 (M<sup>+</sup> - CH<sub>3</sub>, 100). CV:  $E_{ox}$  = 418 mV.

**$t$ -BuNCH<sub>2</sub>CH<sub>2</sub>N( $t$ -Bu)BH (2e).** A mixture of *N,N'*-di-*tert*-butylethylenediamine (3.20 g, 18.6 mmol) and H<sub>3</sub>BNHMe<sub>2</sub> (1.09 g, 18.6 mmol) in toluene (50 mL) was heated under reflux for 4 days. After cooling to room temperature a white precipitate was filtered off, and the filtrate was freed from solvent in vacuo. Crude oily **2e** was purified by distillation at 4 mbar (50–51 °C) to afford 2.54 g (74%) of **2e** as a colorless oil (Found: C, 65.88; H, 12.91; N, 15.36. C<sub>10</sub>H<sub>23</sub>BN<sub>2</sub> requires: C, 65.95; H, 12.73; N, 15.38). <sup>1</sup>H NMR:  $\delta$  1.16 (s, 18H,  $t$ Bu), 3.11 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  30.2 [s, C(CH<sub>3</sub>)<sub>3</sub>], 44.8 (s, CH<sub>2</sub>), 50.1 [s, C(CH<sub>3</sub>)<sub>3</sub>]. <sup>11</sup>B{<sup>1</sup>H} NMR:  $\delta$  26.4 s. <sup>11</sup>B NMR:  $\delta$  26.5 (d, <sup>1</sup>J<sub>BH</sub> = 140 Hz). MS/EI (70 eV):  $m/z$  = 182 (M<sup>+</sup>, 11), 167 (M<sup>+</sup> - CH<sub>3</sub>, 100). CV:  $E_{ox}$  = 662 mV.

**$t$ -BuNCH<sub>2</sub>CH<sub>2</sub>N( $t$ -Bu)BSMe (2f).** A solution of compound **2h** (1.00 g, 3.80 mmol) in hexane (40 mL) was combined with a slurry of NaSMe (1.87 g, 6.00 mmol) in 20 mL of hexane. The resulting mixture was stirred for 10 days at room temperature. It was filtered and the filtrate was freed from solvent in vacuo. The oily residue was distilled by means of a heat gun at 10<sup>-3</sup> mbar to yield 0.73 g (83%) of **2f** as a colorless, viscous oil (Found: C, 58.61; H, 11.33; N, 11.88. C<sub>11</sub>H<sub>25</sub>BN<sub>2</sub>S requires: C, 57.89; H, 11.04; N, 12.28). <sup>1</sup>H NMR:  $\delta$  1.42 (s, 18H,  $t$ Bu), 2.03 (s, 3H, SCH<sub>3</sub>), 3.07 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  13.4 (s, SCH<sub>3</sub>), 30.4 [s, C(CH<sub>3</sub>)<sub>3</sub>], 44.9 (s, CH<sub>2</sub>), 50.2 [s, C(CH<sub>3</sub>)<sub>3</sub>]. <sup>11</sup>B{<sup>1</sup>H} NMR:  $\delta$  31.6 s. MS/EI (70 eV):  $m/z$  = 228 (M<sup>+</sup>, 27), 213 (M<sup>+</sup> - CH<sub>3</sub>, 100). CV:  $E_{ox}$  = 790 mV.

**$t$ -BuNCH<sub>2</sub>CH<sub>2</sub>N( $t$ -Bu)BSnMe<sub>3</sub> (2g).** A slurry of lithium powder (0.15 g, 21.62 mmol) in 10 mL of THF was sonicated for 30 min. Then another portion of 30 mL of THF and 1.13 g (5.67 mmol) of solid trimethyltin chloride was added with vigorous stirring. A solution of **2h** (1.48 g, 5.67 mmol) in 25 mL of hexane was added dropwise to this mixture. Stirring was continued overnight. Thereafter volatiles were removed in vacuo and the residue was triturated with hexane. It was filtered, and the filtrate was evaporated to dryness. The residue was distilled at 10<sup>-3</sup> mbar by means of a heat gun to afford **2g** as a colorless, viscous oil, yield 0.70 g (36%) (Found: C, 45.33; H, 8.83; N, 8.79. C<sub>13</sub>H<sub>31</sub>BN<sub>2</sub>Sn requires: C, 45.25; H, 9.06; N, 8.12). <sup>1</sup>H NMR:  $\delta$  0.23 (s, 9H, SnMe<sub>3</sub>), 1.24 (s, 18H,  $t$ Bu), 2.92 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  -10.2 [s, Sn(CH<sub>3</sub>)<sub>3</sub>], 29.9 [s, C(CH<sub>3</sub>)<sub>3</sub>], 44.5 (s, CH<sub>2</sub>), 51.6 [s, C(CH<sub>3</sub>)<sub>3</sub>]. <sup>11</sup>B{<sup>1</sup>H}

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NMR:  $\delta$  27.3 s. MS/EI (70 eV):  $m/z$  = 331 ( $M^+$  -  $\text{CH}_3$ , 70).  
CV:  $E_{\text{ox}}$  = 754 mV.

**${}^t\text{BuNCH}_2\text{CH}_2\text{N}({}^t\text{Bu})\text{BCN}$  (2i).** A sample of silver cyanide (0.54 g, 4.00 mmol) was added to the solution of compound **2h** (1.00 g, 3.80 mmol) in acetonitrile (40 mL). The slurry was stirred in the dark for 6 h. Volatiles were removed in vacuo, and the residue was triturated with hexane ( $3 \times 20$  mL). The combined hexane extracts were filtered and freed from solvent in vacuo to afford pure **2i** as a colorless solid, yield 0.76 g (96%)

(Found: C, 63.56; H, 10.95; N, 20.09.  $\text{C}_{11}\text{H}_{22}\text{BN}_3$  requires: C, 63.79; H, 10.70; N, 20.29).  ${}^1\text{H}$  NMR:  $\delta$  1.16 (s, 18H,  ${}^t\text{Bu}$ ), 2.79 (s, 4H,  $\text{CH}_2$ ).  ${}^{13}\text{C}\{{}^1\text{H}\}$  NMR:  $\delta$  30.0 [s,  $\text{C}(\text{CH}_3)_3$ ], 45.1 (s,  $\text{CH}_2$ ), 51.6 [s,  $\text{C}(\text{CH}_3)_3$ ].  ${}^{11}\text{B}\{{}^1\text{H}\}$  NMR:  $\delta$  18.9 s. MS/EI (70 eV):  $m/z$  = 207 ( $M^+$ , 21), 192 ( $M^+$  -  $\text{CH}_3$ , 100). CV:  $E_{\text{ox}}$  = 1164 mV.

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