

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

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Authors: Wen-Xiong Zhang, Nan Li, Botao Wu, Chao Yu, Tianyu Li, and Zhenfeng Xi

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201916651 Angew. Chem. 10.1002/ange.201916651

Link to VoR: http://dx.doi.org/10.1002/anie.201916651 http://dx.doi.org/10.1002/ange.201916651

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Trishomoaromatic (B₃N₃Ph₆)-Dianion: Characterization and Two-Electron Reduction

Nan Li,^{#[a]} Botao Wu,^{#[a]} Chao Yu,^[a] Tianyu Li,^[b] Wen-Xiong Zhang*^[a] and Zhenfeng Xi*^[a]

Dedicated to the 100th Birthday of Professor Youqi Tang

Abstract: Benzene, as a common aromatic compound, can be converted to an unstable antiaromatic 8π -electron intermediate through two-electron reduction. However, as an isoelectronic equivalent of benzene, borazine (B₃N₃R₆) of weak aromaticity undergoes the totally different two-electron reduction to afford (B₃N₃R₆)² homoaromatic compounds. Here we report the synthesis of homoaromatic (B₃N₃Ph₆)-dianion by the reduction of B₃N₃Ph₆ with potassium or rubidium in the presence of 18-crown-6. Theoretical investigation illustrates that two electrons delocalize over three boron atoms in (B₃N₃Ph₆)², which is formed by the geometric and orbital reorganization and exhibits (π , σ)-mixed homoaromaticity. Moreover, (B₃N₃Ph₆)-dianion can act as a robust 2e reductant for unsaturated compounds, such as anthracene, chalcone and tanshinones. This 2e reduction is of high efficiency, selectivity, mild conditions and regeneration of neutral borazine.

Aromaticity is an important and fascinating concept in organic chemistry.^[1,2] Benzene is a common aromatic compound with planar **D**_{6h} structure, which can be converted to dearomatized 1,4cyclohexadiene by a classic Birch reduction. Theoretically, benzene could turn into an unstable antiaromatic intermediate (6C, 8π -electron) through two-electron reduction. This may lead to rapid distortion of this intermediate based on pseudo-Jahn-Teller effect, and form a C_2 -symmetric dearomatized dianion eventually (Scheme 1A).^[3] To maintain aromaticity of benzene, four-electron reduction is required.^[4] Borazine, as an isoelectronic equivalent of benzene, has a planar D_{3h} structure and equalized B-N bond lengths (1.44 Å).^[5,6] Despite bearing similar electronic structure, the aromaticity of borazine is a long-controversial topic in history. Up to now, it is widely accepted that borazine shows weak aromaticity due to its limited π -electron delocalization caused by the electronegativity difference between boron and nitrogen atoms.^[5] This structural feature provides many unique properties for borazine, which is remarkably different from benzene. Although the reductions of arenes have been well studied, the reductions of borazine and its derivatives still remain a mystery. Herein, for the first time, we report the two-electron reduction of borazine (B₃N₃Ph₆) via potassium or rubidium in the presence of

[a] Dr. N. Li, Mr. B. Wu, Mr. C. Yu, Prof. Dr. W.-X. Zhang, Prof. Dr. Z. Xi.
Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871 (China)
Fax: (+86)10-62751708
E-mail: wx_zhang@pku.edu.cn; zfxi@pku.edu.cn
[b] Ms. T. Li, College of Chemistry, Beijing Normal University
These authors contributed equally to this work.
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18-Crown-6 to yield (B₃N₃Ph₆)-dianion. Single-crystal X-ray diffraction analysis reveals that it has a **C**_{3v}-symmetric parallel double-layer structure (Scheme 1B). Theoretical investigation illustrates that two electrons delocalize over the three boron atoms in (B₃N₃Ph₆)²⁻ and exhibit (π , σ)-mixed homoaromaticity. These results clearly show that borazine can accept two electrons to its two degenerated LUMOs (2*e*") to give an unstable planar intermediate which undergoes geometric and orbital reorganization to give a parallel double-layer (B₃N₃Ph₆)²⁻ structure (Scheme 1B). In addition, (B₃N₃Ph₆)²⁻ can act as a robust 2*e* reductant for unsaturated compounds.



Scheme 1. The 2e reductions of benzene and borazine.



Scheme 2. Synthesis of $(B_3N_3Ph_6)^{2-}$ compounds 2a/2b and 3a/3b.

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As illustrated in Scheme 2, the phenyl-substituted borazine 1 was synthesized according to the literature procedure.^[7] Treatment of 1 with potassium in THF at RT for 6 h gave a dark red solution. The expected ionic compound 2a was formed in 92% NMR yield as tan solids after THF removal. When 18-Crown-6 (18C6) was added to the above solution of 2a, the corresponding 18C6-coordinated red crystals 3a was obtained in 60% yield. 3a could also be synthesized by successively adding potassium and 18-Crown-6 to the solution of 1. Similarly, the rubidium componds 2b and 3b were obtained in 94% and 64% yields, respectively. Borazines with alkyls on either N or B atoms could not be reduced by alkali metals, which can be attributed to both electronic and spatial effects (for experimental and DFT details, see SI). The reduction reaction occurred with the similar phenomenon to borazine B₃N₃Ph₆ when borazine with p-ethylphenyl on N atoms was used, giving red solids in 70% yield. Due to the low solubility of this red solid in different solvents, we fail to get suitable crystals for X-ray analysis. It can be seen from the above experiments that the phenyl groups are essential for reduction reaction.



Figure 1. Molecular structures of 3a and 3b. Hydrogen atoms, solvent molecules, and the counterions $(M^+)_2(18$ -Crown-6)_2(THF)_2 (M = K or Rb) are omitted for clarity. Selected bond lengths [Å] and angles [°] for 3a: B1-N1 1.508(7), B1-N3 1.513(7), B2-N1 1.493(7), B2-N2 1.520(7), B3-N2 1.520(7), B3-N3 1.485(8), B1-B2 1.983(7), B1-B3 1.971(7), B2-B3 1.997(7), N1-B1-N3 116.4(5), B1-N3-B3 82.2(4); for 3b: B1-N1 1.52(1), B1-N3 1.53(1), B2-N1 1.53(1), B2-N2 1.54(1), B3-N2 1.54(1), B3-N2 1.54(1), B1-B2 2.00(1), B1-B3 2.00(1), B1-B3 1.99(1), N1-B1-N3 114.6(9), B1-N3-B3 81.1(6).

Single-crystal X-ray diffraction analyses reveal that **3a** and **3b** have similar molecular configurations, thus only metric parameters of **3a** is discussed here (Figure 1). In the dianionic fragment of **3a**, three boron atoms and three nitrogen atoms belong to two different planes which are parallel to each other, while the neutral B₃N₃Ph₆ **1** exhibits a planar [B₃N₃] core. The B-N bonds in **3a** [1.485(8)-1.520(7) Å] are slightly longer than those in **1** [1.433(4)-1.447(3) Å].^[7] The distances between two boron atoms (B1-B2 1.983(7) Å, B1-B3 1.971(7) Å, B2-B3 1.997(7) Å) in the [B₃]-plane are significantly longer than typical B-B single bonds (1.72 Å). This comparison shows there is no bond behavior of B-B single bond in **3a**. The angles of N1-B1-N3 and B1-N3-B3 in **3a** are 116.4(5)° and 82.2(4)°, which are different from the neutral one (118.6(2)°, 121.1(2)° for each).

To gain further insight into the electronic structures, DFT calculations and analyses for **3a** were conducted at the B3LYP-D3BJ/def2-TZVP level using Gaussian 16 and Multiwfn.^[8] The orbital interaction was discussed by using the perturbation MO

theory. The optimized geometry is consistent with the X-ray data. Three 2p orbitals of B₃ unit are taken as φ_{a_1} and φ_e (φ_{ex} and φ_{ey}) and three 2p orbitals of N₃ unit are taken as ϕ_{a1} and ϕ_e (ϕ_{ex} and ϕ_{ey}). As shown in Figure 2, both ψ_{1e} and ψ_{2e} are composed of ϕ_{e} and $\varphi_e [\psi_{1e} = \phi_e + \lambda \varphi_e, \psi_{2e} = \varphi_e - \lambda' \phi_e, (0 < \lambda, \lambda' < 1)]$, and φ_{a1} interacts with ϕ_{a1} to constitute ψ_{1a1} and ψ_{2a1} . Although the orbital behavior of C_{3v} -symmetried $(B_3N_3Ph_6)^{2-}$ is similar to borazine, its electron configuration is different. Compared with **D**_{3h}-symmetried</sub> borazine, the energy level of ψ_{2a1} in $(B_3N_3Ph_6)^{2-}$ is lower than ψ_{2a} (in borazine: $\psi_{2a2''}$ and $\psi_{2a''}$). This is caused by the directivity of orbitals' interaction under unique geometric restraints, reflecting the special conjugated effect between N and B atoms. To be specific, ψ_{1a1} reveals negative conjugated interactions by antiphase overlap of B, N-p orbitals, which can be illustrated by the angle of antiphase p orbitals (61° measured) of B and N atoms. Instead, the p-conjugated interaction between N and B atoms turns to be positive in ψ_{2a1} due to the same phase interaction. Compared with ψ_{1a1} , more bonding orbital characteristics are found in ψ_{2a1} and it shows a stabilizing effect, thus reducing the energy level of ψ_{2a1} . This special interactions between B, N-p orbitals result in ψ_{2a1} possessing two electrons as the HOMO of (B₃N₃Ph₆)²⁻, which is much different from trishomoaromatic dianions of 1,3,5-triboracyclohexanes that only p orbitals of B atoms participate in the bonding.[9]



Figure 2. (a) Schematic π -FMO diagrams of theoretical $C_{3\nu}$ -(B₃N₃Ph₆)²⁻ system. Mulliken symbols are used for showing molecular orbitals; (b) The orbital diagrams of $C_{3\nu}$ -(B₃N₃Ph₆)²⁻ system. The isovalue of ψ_{2a} , ψ_{1a} and ψ_{1a1} is 0.05, while the isovalue of ψ_{2a} is 0.03 for clarity. Orange and blue dots represent B and N atoms, respectively. The phenyls on B, N atoms are omitted for clarity.

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In two-electron occupied ψ_{2a1} , apart from conjugated interactions between B and N atoms, there is also a multicenter interaction among three B atoms. Localized Orbital Locator (LOL) function map shows electrons delocalized among three B atoms (Figure 3a). An atoms-in-molecules (AIM) analysis presents the existence of a bond critical point (BCP) at the B₃ center (Figure 3b). Meanwhile the dotted lines around the BCP represent the electron delocalized area. These results demonstrate a 3c-2e interaction in the B₃ center obviously. The multicentered bond order is 0.571, which further proves the 3c-2e bond. The $NICS(0)_{ZZ}$ and $NICS(1)_{ZZ}$ of the B₃ unit are -11.55 and -8.78 ppm, which indicate homoaromatic characters. The angle of 25.5° between the axes of B p-orbitals and the center of the B₃ plane reflects the (π,σ) -mixed homoaromaticity, which shows asymmetric NICS values with respect to the plane of the centers of cyclic delocalization (Figure 3c). It could also be verified in NICS(Z)_{ZZ} curve (Figure 3d).^[10] The NICS minimum is only located at 42 pm above the plane of the centers. The homoaromaticity of B_3 unit could be further verified by the induced current visualization (Figure 3e). It shows that the diamagnetic current appears on the B3 plane to resist the external magnetic field. Thus, (π,σ) -mixed homoaromaticity in **3a** is significantly different from these reported Hückel π B₃ systems,^[11] monohomoaromatic B_3 systems,^[12] (π + σ)-double aromatic B_3 systems, $^{[13]}\sigma\text{-aromatic}\ B_3$ systems $^{[14]}$ and others. $^{[15]}$



Figure 3. Theoretical analysis of $(B_3N_3Ph_6)^{2^-}$ shown as (a) LOL contour map on the Z = 1.0 Bohr over the B_3 plane; (b) The topology of the ∇^2_{Pelec} on the Z = 1.0 Bohr over the B_3 plane; (c) The angle between the axes of B p-orbitals and the center of the B_3 plane is 25.5°; (d) The distribution of NICS(Z)zz values; (e) The induced current sectional view of the Z = 1 Bohr over the B_3 unit.

Absorption, excitation and emission spectra of **3a** and **3b** were also investigated (for details, see SI). Compared with **1** (250-300 nm absorption range),^[7] **3a** and **3b** undergo bathochromic shifts to give absorption range at 325-400 nm, 330-475 nm respectively. As for the steady-state excitation spectrum, **3a** and **3b** display almost the same excitation maxima at 354 nm. In the PL spectrum, **3a** and **3b** show fluorescence at 473 nm and 489 nm individually. The steady-state excitation data correspond well with the simulated results calculated under (TD)PBE0/6-311G^{**} level of theory.^[16] The calculation results show that (B₃N₃Ph₆)²⁻ has the characteristic of valence electronic transition (HOMO→LUMO), and its S1 is close to doublet degeneracy.

Taking 2a as example, the applications of (B₃N₃Ph₆)²⁻ homoaromatic compounds as a 2e reductant were depicted in Table 1. Gratifyingly, the homogeneous reaction between anthracene 4a and 2a/diphenylamine proceeded efficiently at room temperature, giving the desired dihydro compound 4b in 91% yield.^[17] As a contrast, under the heterogeneous condition of K/diphenylamine, the reaction rate decreased obviously. For chalcone **5a** with α , β -unsaturated carbonyl moiety, the reduction took place smoothly, affording 1,3-diphenyl-1-propanone 5b in 90% yield. Natural products like tanshinone I 6a and tanshinone IIA 7a were treated with 2a to lead to the formation of the corresponding phenolic compounds 6b (93% yield) and 7b (95% yield). It is worth mentioning that the neutral B₃N₃Ph₆ could be readily recovered by flash column chromatography after the above reduction reaction. In all, 2a as a robust 2e reductant shows excellent efficiency in reducing unsaturated compounds.



^a Reaction conditions: substrates (0.07 mmol), reductant **2a** (0.077 mmol), THF (5 mL), 5-60 mins, RT. The values in parentheses refer to the yields of isolated product; ^b Diphenylamine (0.154 mmol) as an additive; ^c MeOTf (0.14 mmol) is used to trap diphenol compounds.

In summary, the two-electron reduction of borazine B₃N₃Ph₆ via potassium or rubidium in the presence of 18-Crown-6 is achieved for the first time to yield (B₃N₃Ph₆)-dianion. The (B₃N₃Ph₆)-dianion exhibits the **C**_{3v}-symmetric parallel double-layer structure and the (π , σ)-mixed homoaromaticity. Furthermore, (B₃N₃Ph₆)-dianion can act as a robust 2 ereductant for unsaturated compounds, such as anthracene, chalcone and tanshinones under mild conditions. The unique chemical bonding modes of trishomoaromatic (B₃N₃Ph₆)-dianion disclosed in this work would undoubtedly

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enrich the chemistry of borazine as well as the concept of homoaromaticity.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21725201, 21890721, 21690061). We thank Prof. Shang-Da Jiang and Dr. Zifeng Zhao for the help of experimental measurements. We thank Prof. Shengfa Ye, Prof. Jun Zhu, Dr. Junnian Wei, Dr. Rui Feng and Mr. Zhe Huang for the theoretical discussions. Theoretical calculations of this work was supported by High-performance Computing Platform of Peking University

Keywords: alkali metals • borazine • homoaromaticity • reduction • 3c-2e interaction

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