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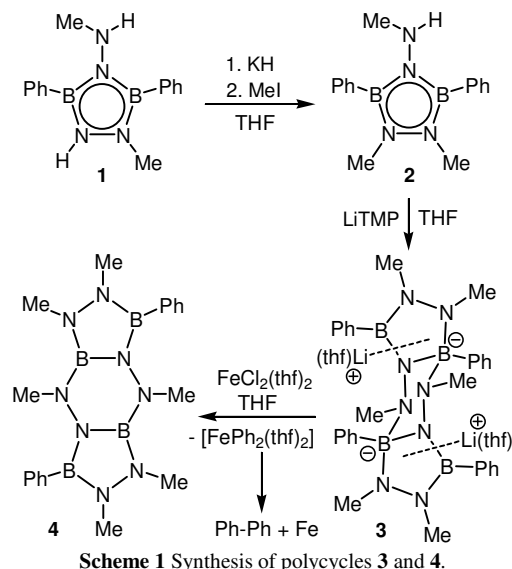
Assembly of a Planar, Tricyclic B₄N₈ Framework With *s*-Indacene Structure

Hanh V. Ly,^a Heikki M. Tuononen,^b Masood Parvez^a and Roland Roesler*^a

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A neutral, formally 16- π -electron, tricyclic tetrahydrazidotetraborane was obtained in a two-step procedure involving self-assembly of a dilithiodiborate with B₄N₈ framework and subsequent oxidation of the phenylborate moieties to boranes and biphenyl using Fe(II) as an oxidant.

The chemistry and properties of borazines, the “inorganic” analogues of benzene, were intensely investigated in the mid sixties.¹ Borazine research has experienced a resurgence in the last few years, driven by the applications as precursors to boron nitride fibres and ceramics,² as well as molecular materials.³ Boron



derivatives of hydrazines have received considerably less attention. However, a few cyclic tetraazadiborinanes have been synthesized and structurally characterized.⁴ A limited number of molecules with bi and tricyclic BN frameworks have been reported as well,⁵ including analogues of phenalene,^{5b} naphthalene^{5f} and Dewar benzene.^{5e}

We were interested in studying the ligand properties of the planar 6- π -electron system **1**,^{6a} which was obtained through quantitative self-assembly of monomethylhydrazine with PhB(NMe₂)₂, according to a reported procedure.^{6b} Deprotonation of

1 with KH followed by methylation with MeI resulted in clean replacement of the more acidic ring proton in **1** with a methyl group. The disappearance of the signal corresponding to the ring proton of **1** at 7.48 ppm in the ¹H NMR spectrum clearly indicated

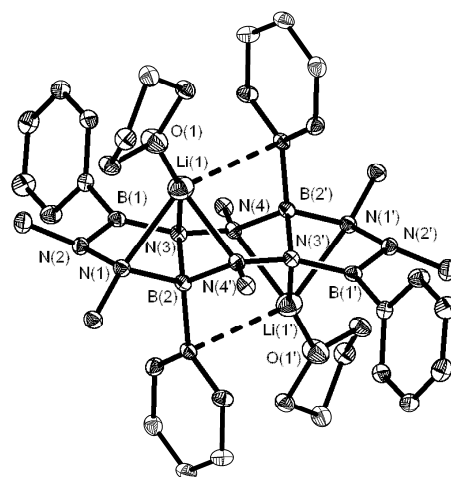


Fig. 1 Molecular structure of **3** with 50 % probability level thermal ellipsoids. Hydrogen atoms on the organic substituents have been omitted for clarity and atoms marked with a prime (') character are at equivalent position (-x, -y, 1-z). Selected bond lengths (Å): B(1)-N(2) 1.441(2), B(1)-N(3) 1.408(2), B(2)-N(1) 1.562(2), B(2)-N(3) 1.556(2), B(2)-N(4') 1.566(2), N(1)-N(2) 1.475(2), N(3)-N(4) 1.445(2), Li(1)-N(1) 2.189(3), Li(1)-N(3) 2.326(3), Li(1)-N(4') 2.035(3), Li(1)-O(1) 1.902(3), Li(1)···C(10') 2.775(3), B(1)-C(4) 1.579(2), B(2)-C(10) 1.636(2), N-C 1.446(2) – 1.462(2).

the regiochemistry of the reaction. The lithium amide produced by deprotonation of the exocyclic nitrogen in **2** with LiTMP dimerized through N-B bond formation, producing the dilithium salt of a tricyclic borate dianion **3**. The ¹H and ¹³C NMR spectra confirmed the presence of two inequivalent phenyl groups and three inequivalent methyl groups, while the ¹¹B NMR spectrum featured signals corresponding to the borane and the borate moieties at 28.5 and 2.7 ppm, respectively. The chemical shift of the ⁷Li NMR signal (-2.18 ppm) is typical for Li(thf)₄⁺, suggesting the presence of solvent separated ion pairs in THF solution.⁷

A crystallographic determination for **3** revealed a centrosymmetric structure featuring a tricyclic, annelated B₄N₈ skeleton containing two B₂N₃ rings connected through a B₂N₄ ring (Figure 1). As indicated by the NMR spectra, the skeleton contains two borane and two borate moieties. The tetracoordinated boron, B(2) is situated 0.6 Å outside the best plane formed by the other skeletal atoms, determining the envelope conformation of the five

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membered rings (folding angle along the N(1)⋯N(3) axis ca. 30°) and the chair conformation of the six membered ring (folding angle along the N(3)⋯N(4') axis ca. 55°). The N-N bond lengths are 1.443(2) and 1.475(2) Å, comparable to the N-N bond length in hydrazine (1.45 Å).⁸ The B-N bonds involving the borane center

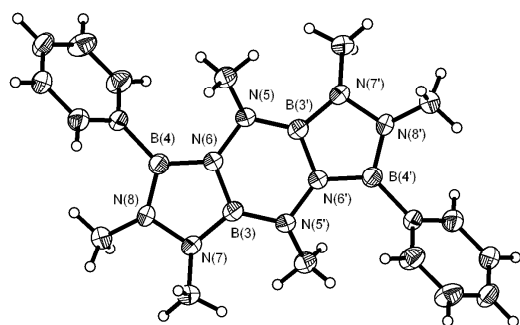


Fig. 2 One of the two independent molecules in the structure of **4** with 50 % probability level thermal ellipsoids. Atoms marked with a prime (') character are at equivalent position (-x, 2-y, -z). Selected bond lengths (Å) and angles (°); calculated values are reported in square brackets: B-N 1.423(3) – 1.440(3) [1.429 – 1.440], N-N 1.436(2) – 1.441(2) [1.411 – 1.416], N-C 1.446(3) – 1.463(3) [1.440 – 1.447], C-B 1.556(3) [1.565], 1.570(3) [1.565], B(3')-N(5)-N(6) 113.72(15) [113.5], N(5)-N(6)-B(3) 122.09(15) [122.2], N(6)-B(3)-N(5') 124.18(18) [124.2], B(3)-N(6)-B(4) 108.26(17) [108.0], N(6)-B(4)-N(8) 106.85(17) [106.7], B(4)-N(8)-N(7) 109.49(15) [109.8], N(8)-N(7)-B(3) 106.70(15) [107.1], N(7)-B(3)-N(6) 108.35(16) [108.1].

B(1) (1.408(2) and 1.441(2) Å) are much shorter than those involving the borate center B(2) (1.556(2) – 1.566(2) Å). The lithium ions are positioned 1.7 Å outside the best plane of the ligand, and are coordinated by the three nitrogen atoms connected to the borate center. The coordination sphere of the lithium ion is completed by an intramolecular contact involving the ipso carbon of the phenylborate moiety, and a THF molecule.

Oxidation of **3** with FeCl₂(thf)₂ in THF produced the neutral BN tricycle **4** in low (22 %) but reproducible isolated yield. The other probable product of this reaction, FePh₂(thf)₂, subsequently decomposed to metallic iron and biphenyl, which were identified in the reaction mixture. A similar decomposition pathway was reported for FePh₂(PEt₃)₂ at temperatures above 0 °C.⁹ The ¹H and ¹³C NMR spectra of **4** featured the resonances expected for one phenyl group and three inequivalent methyl groups, and the signals corresponding to the two inequivalent boron centers merged into a broad singlet at 25.1 ppm. The use of a stoichiometric quantity of I₂ as oxidizing agent instead of FeCl₂(thf)₂ did not result in the formation of **4**. The electrochemical oxidation of tetraphenylborate to boric acid and biphenyl in aqueous conditions at a potential of 0.216 V vs. SCE has been reported,¹⁰ however, the reaction of Li[BPh₄] with FeCl₂(thf)₂ failed to produce BPh₃. Thus, the formation of the stable polycycle appears to be an essential thermodynamic contributor to the oxidation of the phenylborate **3** to biphenyl and the borane **4**.

The X-ray diffraction study of **4** reveals two very similar, centrosymmetric, independent molecules containing planar B₄N₈ frameworks with *s*-indacene structure (Figure 2). The tricyclic skeleton is regular, with all B-N and N-N bonds having the same length, between 1.423(3) and 1.441(2) Å. This length is characteristic of a partial multiple bond character for N-B, as observed in borazines (1.42 – 1.44 Å),¹¹ and for a single N-N bond

(vide supra). The phenyl substituents show little deviation from the ring plane (5.3°), while the C-N bonds form angles of 22.7 – 31.1° with this plane, in an all-trans arrangement. The all-carbon analog of **4**, *s*-indacene, is an unstable molecule with formally antiaromatic character according to the Hückel rule (12- π -electrons).¹² Its more stable substituted derivatives¹³ can be reduced to formally aromatic, 14- π -electron dianions.¹⁴ It could therefore be expected that a two electron oxidation or reduction of **4** would yield a stable dication or dianion, respectively, satisfying the Hückel condition of aromaticity. In order to investigate this hypothesis, theoretical investigations were performed for **4** as well as for its doubly reduced and oxidized forms.¹⁵

The geometry optimized structure of **4** is in excellent agreement with the data from the structural determination (Figure 2). The analysis of Kohn-Sham orbitals of **4** confirms that it is only formally a 16- π -electron system: though the tricyclic B₄N₈ framework is essentially planar, the geometry around all methyl substituted nitrogen atoms is pyramidal, giving rise to MOs with only partial π -like character (see Electronic Supplementary Information). The HOMO is π -antibonding through all four N-N linkages, which readily explains the observed long bond distances indicative of single bonds.

The B₄N₈ framework is significantly nonplanar in the anion [**4**]²⁻ due to occupation of a MO with B-N antibonding character. Hence, a two-electron reduction of **4** leads to a structure which does not fulfill the general conditions of aromaticity. On the other hand, the two-electron oxidation of **4** yields a dication with a nearly planar structure because two electrons are removed from the N-N antibonding HOMO (see Electronic Supplementary Information). The minor geometric distortions present in the system arise from steric interactions, as evidenced by the geometry optimized structure of a hydrogen substituted tricycle [B₄N₈H₈]²⁺, displaying a perfectly planar Hückel aromatic geometry. Interestingly, the closed shell singlet state SCF solution of [**4**]²⁺ has an internal instability indicating that the singlet ground state of this dication has nitrogen-centered diradical character. Hence, the open-shell singlet diradical state of [**4**]²⁺ was modeled using broken symmetry formalism and the calculated structure was compared to the lowest energy triplet state. The calculations showed that the two spin states are very close in energy, with the formally aromatic open-shell singlet state being ca. 5 kJ mol⁻¹ lower than the triplet state.

Unfortunately the experimental search for a stable oxidation product of **4** remained fruitless. Cyclic voltammetric measurements were performed in THF in the range of -2.5 to 1.5 V, and they showed two irreversible oxidation steps at 0.35 and 0.90 V vs. SCE (-0.21 and 0.34 V vs. Fc). Chemical oxidation with [Cp₂Fe]PF₆ produced Cp₂Fe and a solid that was insoluble in organic solvents and was not further characterized. Radical species were not detected by EPR upon in-situ electrochemical oxidation. We note that stable radicals with *s*-indacene-like frameworks are well-known in the chalcogen-nitrogen chemistry.¹⁹ This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Canada Foundation for Innovation, the Academy of Finland and the Alberta Science and Research Investments Program. The authors wish to thank Ms. Tracey L. Roemmele and Dr. René T. Boeré for assistance with the EPR and cyclic voltammetric measurements.

Notes and references

- All operations were conducted under strict exclusion of air and moisture. Solvents were dried prior to use and methylhydrazine was dried over CaH₂. Methylated hydrazines are highly toxic and probable carcinogens, and their handling requires special precautions; all residues were neutralized using commercial bleach solution.
- Synthesis of 2:** A solution of **1**⁶ (0.700 g, 2.65 mmol) in THF (20 mL) was slowly added to a suspension of KH (0.106 g, 2.65 mmol) in THF (15 mL). KH dissolved with evolution of hydrogen producing a yellow solution that was stirred at ambient temperature for another 2 h. MeI (0.165 mL, 2.65 mmol) was added to the mixture and the colourless suspension was stirred for an additional hour and then concentrated under vacuum to ca. 3 mL. Hexane (30 mL) was added and the KI by-product was filtered off. The solvent was subsequently removed *in vacuo*, leaving behind the product as a colourless powder (638 mg, 88 %). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 2.32 (d, 3H, ³J_{HH} = 6.4 Hz, HNCH₃), 2.88 (s, 6H, (NCH₃)₂), 3.76 (q, 1H, ³J_{HH} = 6.4 Hz, HNCH₃), 7.25 - 7.34 (m, 6H, *m*- + *p*-C₆H₅), 7.74 (d, 4H, ³J_{HH} = 6.6 Hz, *o*-C₆H₅); ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ = 31.7 (s, (NCH₃)₂), 43.5 (s, HNCH₃), 128.8 (s, *m*-C₆H₅), 129.1 (s, *p*-C₆H₅), 134.4 (s, *o*-C₆H₅), 135.0 (s, br, *i*-C₆H₅); ¹¹B NMR (128 MHz, THF-d₈, 25 °C): δ 28.6 (s, br).
- Synthesis of 3:** A solution of lithium 2,2,6,6-tetramethylpiperidide, LiTMP was prepared from 1.6 M *n*-butyllithium in hexane (1.12 mL, 1.80 mmol) and tetramethylpiperidine, TMP, (0.254 g, 1.80 mmol) in THF (3 mL). The solutions of **2** (0.500 g, 1.80 mmol) in THF (3 mL) and LiTMP were pre-cooled to -35 °C and mixed, yielding an orange solution that was stored at -35 °C for a day. Subsequently it was allowed to warm to room temperature and volatiles were removed *in vacuo*, leaving behind a yellow residue that was washed twice with hexane (30 mL) and dried under vacuum. The product was obtained as a colourless powder (388 mg, 60.5 %). ¹H NMR (400 MHz, THF-d₈, 25 °C): δ 2.01 (s, 6H, NCH₃), 2.28 (s, 6H, NCH₃), 2.71 (s, 6H, NCH₃), 7.12 - 7.31 (m, 12H, *m*- and *p*-C₆H₅), 7.53 (d, 4H, ³J_{HH} = 6.8 Hz, *o*-C₆H₅), 7.77 (d, 4H, ³J_{HH} = 6.8 Hz, *o*-C₆H₅); ¹³C NMR (100 MHz, THF-d₈, 25 °C): δ 34.2 (s, NCH₃), 39.1 (s, NCH₃), 41.3 (s, NCH₃), 126.3 (s, *p*-C₆H₅), 127.2 (s, *p*-C₆H₅), 127.5 (s, *m*-C₆H₅), 128.0 (s, *m*-C₆H₅), 134.0 (s, *o*-C₆H₅), 135.9 (s, *o*-C₆H₅); ¹¹B NMR (128 MHz, THF-d₈, 25 °C): δ = 2.7 (s) and 28.5 (s, br); ⁷Li NMR (155 MHz, THF-d₈, 25 °C): δ -2.18 (s). Needle-like X-ray quality crystals were obtained by recrystallization of **3** from THF.
- Synthesis of 4:** A solution of **3** (80.0 mg, 0.112 mmol) in THF (3 mL) was added to solid FeCl₂(thf)₂²⁰ (38.0 mg, 0.141 mmol). The dark mixture was allowed to stand at room temperature for a day, and was then concentrated to 1 mL and cooled to -35 °C for several days until colourless crystals of **4** formed and were separated by decantation (10 mg, 22 %). ¹H NMR (400 MHz, THF-d₈, 25 °C): δ 2.66 (s, 6H, NCH₃), 2.83 (s, 6H, NCH₃), 2.87 (s, 6H, NCH₃), 7.31 - 7.33 (m, 6H, *m*- and *p*-C₆H₅), 7.55 (d, 4H, ³J_{HH} = 5.6 Hz, *o*-C₆H₅); ¹³C NMR (100 MHz, THF-d₈, 25 °C): δ 32.9 (s, NCH₃), 33.7 (s, NCH₃), 42.4 (s, NCH₃), 128.4 (s, *m*-C₆H₅), 128.9 (s, *p*-C₆H₅), 134.2 (s, *o*-C₆H₅); ¹¹B NMR (128 MHz, THF-d₈, 25 °C): δ 25.1 (s, br); MS (EI+, 70 eV): *m/z*(%): 400(51) [M]⁺, 385(13) [M - Me]⁺, 278(40) [M - Ph - 3Me]⁺, 154(41) [B₄N₈]⁺; HRMS for H₂₈C₁₈N₈¹¹B₄: calcd. 400.2809, found 400.2838.
- Crystal data for 3:** C₃₈H₅₄B₄Li₂N₈O₂, *M* = 712.02, monoclinic, space group *P*2₁/*n*, *a* = 13.149(5), *b* = 9.299(4), *c* = 16.145(6) Å, β = 100.17(3)°, *V* = 1943.1(13) Å³, *Z* = 2, *D_c* = 1.217 g cm⁻³, *F*(000) = 760, μ(Mo-Kα) = 0.074 mm⁻¹, λ = 0.71073 Å, *T* = 123(2) K. 8425 reflections measured, 4398 unique data (2θ_{max} = 55.0°, *R*_{int} = 0.027). GOF on *F*² = 1.02, w*R*₂(*F*²) = 0.126 for all data, *R*₁(*F*) = 0.047 on reflections having *I* > 2σ(*I*). CCDC # 649697.
- Crystal data for 4:** C₁₈H₂₈B₄N₈, *M* = 399.72, triclinic, space group *P*-1, *a* = 17.240(3), *b* = 9.157(6), *c* = 16.983(12) Å, α = 75.88(3)°, β = 83.19(4)°, γ = 76.55(4)°, *V* = 1059.7(11) Å³, *Z* = 2, *D_c* = 1.253 g cm⁻³, *F*(000) = 424, μ(Mo-Kα) = 0.077 mm⁻¹, λ = 0.71073 Å, *T* = 173(2) K. 6791 reflections measured, 3693 unique data (2θ_{max} = 50.0°, *R*_{int} = 0.031). GOF on *F*² = 1.01, w*R*₂(*F*²) = 0.146 for all data, *R*₁(*F*) = 0.046 on reflections having *I* > 2σ(*I*). CCDC # 649698.
- Cyclovoltammetry of 4:** The measurements were performed in THF at an analyte concentration of 1mM, and using 0.1 M [*n*Bu₄N]PF₆ as a supporting electrolyte. A PARstat 2273 potentiostat was used at scan rates between 50 to 1000 mVs⁻¹. The cell had a platinum disk working electrode, a platinum wire auxiliary electrode, and a silver wire pseudo-reference electrode. [Cp₂Co]^{0/+1} with E⁰ = -1.36 V vs. ferrocene and -0.80 V vs. the SCE was used as an internal standard.
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