

A Boron Analogue of Benzene: Synthesis, Structure, and Reactivity of 1-*H*-Boratabenzene

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The 1-*H*-boratabenzene anion is of interest from many perspectives, including structure and electronic character (cf. benzene, Figure 1),¹ as well as reaction chemistry. Although a number of B-substituted boratabenzenes have been prepared,² there has been only one report of a derivative of the parent anion, the work of Ashe, who synthesized Fe(C₅H₅BH)₂.³ In this communication we describe the first structural characterization of a 1-*H*-boratabenzene, specifically, the X-ray crystal structure of the simplest member of this family, lithium 1-*H*-boratabenzene. We also present our initial studies of the reactivity of this species.

Treatment of borabenzene–PMe₃⁴ with 1 equiv of LiAlH₄ in THF at room temperature results in clean conversion⁵ to lithium 1-*H*-boratabenzene (**1**, eq 1).^{6–9} Crystallization of **1**

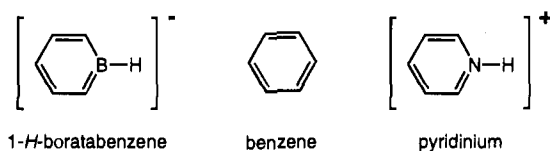


Figure 1. Isoelectronic series.

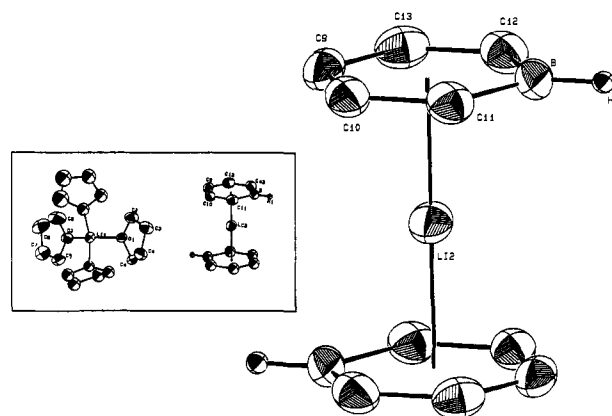
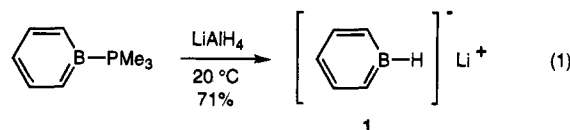


Figure 2. ORTEP drawing of **1**, with thermal ellipsoids drawn at the 35% probability level.

from tetrahydrofuran/toluene/hexane provided colorless crystals suitable for X-ray analysis (Figure 2).¹⁰



As illustrated in Figure 2, lithium 1-*H*-boratabenzene crystallizes as a sandwich complex.¹¹ One lithium ion is positioned at the center of symmetry of the two 1-*H*-boratabenzene rings,¹² and the second lithium ion is coordinated by four THF molecules in a tetrahedral geometry.¹³ The parallel boratabenzene rings are eclipsed relative to one another.

The structure of the boratabenzene ring of **1**, like that of the closely related [(C₅H₅BMe)(NMe₃Ph)]₂,^{2b} is consistent with the heterocycle being aromatic.^{14,15} The ring is planar (all torsion angles are smaller than 1°),¹⁶ and the four carbon–carbon bond distances are comparable to each other (1.38–1.41 Å, Figure 3a), as well as to those of benzene¹⁷ and of pyridinium salts¹⁸ (~1.40 Å). The carbon–boron bond lengths (1.45 and 1.48 Å) are slightly longer than the carbon–carbon bond lengths

(13) A recent NMR study indicates that in THF at low temperature monomeric CpLi is in equilibrium with a dimeric species consisting of a [Cp₂Li][–] sandwich anion and a lithium cation tetrahedrally solvated by THF (Paquette, L. A.; Bauer, W.; Sivik, M. R.; Buhl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776–8789).

(14) For a discussion of the aromaticity of 1-methylboratabenzene, see: Sullivan, S. A.; Sandford, H.; Beauchamp, J. L.; Ashe, A. J., III. *J. Am. Chem. Soc.* **1978**, *100*, 3737–3742.

(15) We are pursuing computational studies of lithium 1-*H*-boratabenzene (M. DiMare, University of California at Santa Barbara, unpublished results). For computational studies of free borabenzene (C₅H₅B) and of neutral borabenzene–ligand adducts, see: (a) Schulman, J. M.; Disch, R. L.; Sabio, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 3785–3788. (b) Raabe, G.; Heyne, E.; Schleker, W.; Fleischhauer, J. *Z. Naturforsch., A* **1984**, *39*, 678–681. (c) Raabe, G.; Schleker, W.; Heyne, E.; Fleischhauer, J. *Z. Naturforsch., A* **1987**, *42*, 352–360. (d) Schulman, J. M.; Disch, R. L. *Organometallics* **1989**, *8*, 733–737. (e) Cioslowski, J.; Hay, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 1707–1710.

(16) Significant deviations from planarity have been observed for some transition metal complexes of B-substituted boratabenzenes (see ref 2a).

(17) Cox, E. G.; Cruickshank, D. W. J.; Smith, J. A. S. *Nature* **1955**, *175*, 766.

(18) For example, see: (a) Zaworotko, M. J.; Cameron, T. S.; Linden, A.; Sturge, K. C. *Acta Crystallogr.* **1989**, *C45*, 996–1002. (b) Copeland, R. F.; Conner, S. H.; Meyers, E. A. *J. Phys. Chem.* **1966**, *70*, 1288–1296.

(1) For reviews of aromaticity and heteroaromaticity, see: (a) Simkin, B. Y.; Minkin, V. I.; Glukhovtsev, M. N. *Adv. Heterocycl. Chem.* **1993**, *56*, 303–428. (b) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; Wiley: New York, 1994. See also: Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337–340.

(2) (a) For an early review, see: Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199–236. (b) For a comprehensive discussion of recent progress in the chemistry of lithium boratabenzene derivatives, see: Herberich, G. E.; Schmidt, B.; Englert, U. *Organometallics* **1995**, *14*, 471–480.

(3) (a) Ashe, A. J., III; Butler, W.; Sandford, H. F. *J. Am. Chem. Soc.* **1979**, *101*, 7066–7067. (b) For computational studies, see: Kostic, N. M.; Fenske, R. F. *Organometallics* **1983**, *2*, 1319–1325. Clack, D. W.; Warren, K. D. *J. Organomet. Chem.* **1981**, *208*, 183–188 and earlier papers in this series.

(4) Borabenzene–PMe₃ was prepared by a route similar to that described for the synthesis of borabenzene–pyridine (Boese, R.; Finke, N.; Henkelmann, J.; Maier, G.; Paetzold, P.; Reisenauer, H. P.; Schmid, G. *Chem. Ber.* **1985**, *118*, 1644–1654).

(5) The yield is greater than 95% by NMR (versus an internal standard).

(6) Despite its dimeric structure in the solid state (vide infra), for the sake of simplicity we refer to the reaction product as lithium 1-*H*-boratabenzene (**1**). Studies of the solution phase structure of **1** are underway.

(7) To the best of our knowledge, this is the first example of a borabenzene–(neutral ligand) adduct undergoing ligand substitution. We are currently exploring the scope and the mechanism of this process.

(8) For routes to B-substituted lithium boratabenzenes, see: (a) Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804–1805. (b) Ashe, A. J., III; Meyers, E.; Shu, P.; Von Lehmann, T.; Bastide, J. *J. Am. Chem. Soc.* **1975**, *97*, 6865–6866. (c) Herberich, G. E.; Schmidt, B.; Englert, U.; Wagner, T. *Organometallics* **1993**, *12*, 2891–2893. (d) Reference 2b. (For a route to B-substituted sodium and potassium boratabenzenes, see: Herberich, G. E.; Becker, H. J.; Carsten, K.; Koch, W. *Chem. Ber.* **1976**, *109*, 2382–2388.)

(9) ¹H NMR (300 MHz, d₈-THF): δ 7.19 (dd, 2H, J₁ = 8.8 Hz, J₂ = 7.4 Hz, meta H), 6.57 (ddt, 2H, J₁ = 10.2 Hz, J₂ = 4.8 Hz, J₃ = 1.4 Hz, ortho H), 6.21 (td, 1H, J₁ = 7.1 Hz, J₂ = 1.4 Hz, para H), 5.5–4.0 (br, 1H, B–H). ¹³C NMR (75 MHz, d₈-THF): δ 133.3, 128.2 (br), 111.8. ¹¹B NMR (96 MHz, d₈-THF; referenced to neat BF₃·OEt₂ at δ 0.0): δ 32. ⁷Li NMR (116 MHz, d₈-THF, 0.53 M; referenced to 1.0 M LiBr in H₂O at δ 0.0): δ –4.2. IR (KBr): 2497 cm^{–1} (B–H).

(10) X-ray data for **1**: Data were collected using the ω scan technique on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation, operating at –86 ± 1 °C. The crystal is monoclinic [C₂/c (No. 15)]; a = 16.213(2) Å, b = 8.403(2) Å, c = 20.775(4) Å; β = 95.15(1)°; V = 2819(2) Å³; Z = 4, FW = 456.13, ρ(calcd) = 1.075 g/cm³. The structure was solved by direct methods and refined by full-matrix least squares to R = 0.062; R_w = 0.055. The location of the boron atom was determined through the use of comparative thermal parameters.

(11) The B–H bond length is 0.94(3) Å.

(12) Structurally related transition metal complexes of B-substituted boratabenzene derivatives are known (for examples, see ref 2a). The only lithium boratabenzene derivative that has been characterized crystallographically does not adopt a sandwich structure ([Li{Me₂N(CH₂)₃NMe₂}]₂(C₅H₅BNMe₂); ref 8c).

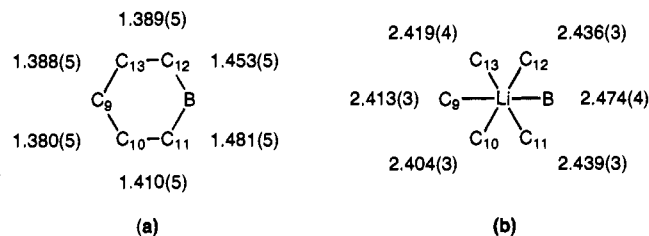


Figure 3. Interatomic bond distances in angstroms.

(1.38–1.41 Å) (Figure 3a), consistent with the larger covalent radius of boron versus carbon.¹⁹ The intraannular bond angles range from 116° to 122°.

The sandwiched lithium ion of **1** lies above the B–C_{9(para)} axis and is slightly displaced from the centroid of the ring, toward the para carbon (Figure 3b). The magnitude of this displacement is significantly less than that observed in the only reported structure of a lithium boratabenzene derivative, [Li–{Me₂N(CH₂)₃NMe₂}] (C₅H₅BNMe₂).^{8c} Herberich has suggested that, in the case of the latter complex, the strong interaction between the lone pair on nitrogen and the π symmetry orbital on boron results in a species that more closely resembles a cyclohexadienyl anion than an aromatic one.

A comparison of the structure of lithium 1-*H*-boratabenzene with alkali metallocenes²⁰ is instructive. [Cp₂Li][PPh₄] (“lithocene anion”) has recently been characterized crystallographically.^{21,22} It adopts a sandwich structure, with lithium located at the inversion center of the metallocene, analogous to the situation found for lithium 1-*H*-boratabenzene (Figure 2). In contrast to the eclipsed conformation present in **1**, the rings of [Cp₂Li] anion are staggered. The lithium–centroid distance for lithocene anion is 2.01 Å, comparable to the corresponding

(19) Covalent radii: 0.82 Å (boron), 0.77 Å (carbon). Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; pp 82–83.

(20) For a recent review, see: Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2168–2171. See also: Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1–17.

(21) Harder, S.; Prosenc, M. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744–1746.

(22) Studies of CpLi in solution: (a) Reference 13. (b) Besten, R.; Harder, S.; Brandsma, L. *J. Organomet. Chem.* **1990**, *385*, 153–159.

distance for lithium 1-*H*-boratabenzene (1.98 Å). Interestingly, despite the higher inherent symmetry of a cyclopentadienyl versus a boratabenzene ligand, [Cp₂Li] anion shares with **1** two features noted above: variation in carbon–carbon bond distances (1.34–1.39 Å for [Cp₂Li]) and displacement of the sandwiched lithium ion from the centroid of the aromatic rings (carbon–lithium distances vary from 2.26 to 2.37 Å for [Cp₂Li]).

We have initiated studies of the reactivity of lithium 1-*H*-boratabenzene. The hydridic nature of the boron-bound hydrogen is evident from the reaction of **1** with electrophiles: it reduces *n*-dodecanal to dodecanol, reacts with D₂O to liberate HD, and reductively cleaves the epoxide ring of styrene oxide.²³

In summary, we have provided the first structural characterization, as well as initial reactivity studies, of a 1-*H*-boratabenzene, the boron analogue of benzene. Further investigation of this unique boron hydride is underway.

Note Added in Proof: Treatment of *n*-dodecanal with lithium 1-*D*-boratabenzene cleanly affords 1-deuterio-1-dodecanol.

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Supporting Information Available: Experimental procedures for the synthesis of **1** as well as for reactivity studies, and full X-ray data for **1** (51 pages); observed and calculated structure factors for **1** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(23) The mechanism of these reactions is under investigation.