1,2-Dihydro-1,2-oxaborine: A Boron−Oxygen Heterocycle Isoelectronic with Benzene

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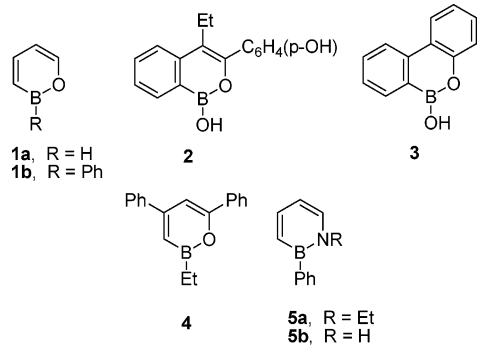
*Summary: 1,2-Dihydro-2-phenyl-1,2-oxaborine (**1b**) has been prepared by the reaction of (2,3-dihydro-1,2-oxaborol-3-yl)-potassium (**8**) with methylene chloride and KN(SiMe$_3$)$_2$. Structural characterization of the phenyl−Cr(CO)$_3$ complex **9** suggests that the 1,2-dihydro-1,2-oxaborine ring has a π-delocalized structure.*

The boron−oxygen heterocycle 1,2-dihydro-1,2-oxaborine (**1**) is a potentially aromatic six-π-electron compound. Several



fused-ring derivatives of **1**, isoelectronic with naphthalene,[1,2] e.g., **2**, and phenanthrene,[3−6] e.g., **3**, have been prepared. Structural data on **2** and **3** show that there are no significant differences between the B−O bond lengths which are exocyclic and endocyclic to the ring.[1,5,6] These B−O bond distances are also not significantly different from those of PhB(OH)$_2$.[7] Thus, the arylboronic acid derivatives **2** and **3** seem to have little π-delocalization over the heterocyclic rings. Unfortunately there are no structural data for compound **4**, which is the only reported non-fused-ring 1,2-dihydro-1,2-oxaborine.[8] Recently ab initio and DFT calculations on **1a** have suggested that 1,2-dihydro-1,2-oxaborines have considerable aromatic stabilization.[9] To experimentally test this hypothesis, a good synthesis of minimally substituted derivatives of **1** would be highly desirable. We report here on a synthesis of 1,2-dihydro-2-phenyl-1,2-oxaborine (**1b**). The availability of **1b** has allowed us to prepare its phenyl−Cr(CO)$_3$ complex **9,** which has been structurally characterized. These data clarify the potential aromaticity of the 1,2-dihydro-1,2-oxaborine ring system.

Our synthesis of **1b** involves an extension of the carbenoid ring-expansion route recently used to prepare the analogous boron−nitrogen heterocycle **5**.[10] The appropriate 1,2-oxaborolide (**8**) needed for the ring expansion was prepared in two steps from the readily available 2,2-dibutyl-2,5-dihydro-1,2-oxastannole (**6**), as illustrated in Scheme 1.[11] The reaction of **8** with excess methylene chloride and KN(SiMe$_3$)$_2$ gave a 35% yield of **1b** as an air-sensitive colorless liquid.[12] When the reaction was performed using methylene chloride-d_2, the deuterium in **1b** was exclusively at the 3-position. The reaction is consistent with an in situ formation of chlorocarbene, followed by addition of the carbene to the position adjacent to boron of **8** and ultimately by ring expansion and loss of chloride as illustrated.[10,13]

The ^{1}H NMR spectrum of **1b** in THF-d_8 shows a first-order pattern, which is consistent with the assigned structure. The ^{1}H,

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(1) Arcus, V. L.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1993**, *460*, 139.

(2) Paetzold, P.; Stanescu, C.; Stubenrauch, J. R.; Bienmüller, M.; Englert, U. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2632.

(3) (a) Dewar, M. J. S.; Dietz, R. *J. Chem. Soc.* **1960**, 1344. (b) Davis, F. A.; Dewar, M. J. S. *J. Org. Chem.* **1968**, *33*, 3324.

(4) (a) Grisdale, P. J.; Williams, J. L. R. *J. Org. Chem.* **1969**, *34*, 1675. (b) Zhou, J. Q.; Worm, K.; Dolle, R. E. *J. Org. Chem.* **2004**, *69*, 5147.

(5) Maringgele, W.; Meller, A.; Noltemeyer, M.; Sheldrick, G. M. *Z. Anorg. Allg. Chem.* **1986**, *536*, 24.

(6) Greig, L. M.; Kariuki, B. M.; Habershon, S.; Spencer, N.; Johnston, R. L.; Harris, K. D. M.; Philip, D. *New J. Chem.* **2002**, *26*, 701.

(7) Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1977**, *55*, 3071.

(8) Köster, R.; Pourzal, A.-A. *Synthesis* **1973**, 674.

(9) Minyaev, R. M.; Minkin, V. I.; Gribanova, T. N.; Starikov, A. G. *Mendeleev Commun.* **2001**, *2*, 43.

(10) Ashe, A. J., III; Fang, X. D.; Fang, X. G.; Kampf, J. W. *Organometallics* **2001**, *20*, 5413.

(11) Chen, J.; Kampf, J. W.; Ashe, A. J., III. *Organometallics* **2004**, *23*, 5088.

(12) Experimental procedures and characterization of new compounds are as follows. **1b**: THF (20 mL) at −78 °C was added slowly via a cannula to a mixture of KN(SiMe$_3$)$_2$ (1.54 g, 7.70 mmol) and **8** (1.33 g, 7.33 mmol) with stirring. Methylene chloride (10 mL) was added slowly at −78 °C. The mixture was stirred at −78 °C for 2 h and then warmed slowly to 25 °C for 10 h. The solvent was removed under reduced pressure, and the residue was extracted with pentane (2 × 25 mL). Removal of the solvent from the extracts gave a dark red oil, which was distilled (32 °C at 0.01 Torr) to afford **1b** as a colorless liquid (0.40 g, 35% yield). IR (film; cm^{-1}): 3075, 3014, 1617, 1504, 1435, 1388, 1266, 740, 697, 678. UV (hexane; λ_{max}, nm): 288, 231, 198. ^{1}H NMR (500 MHz, THF-d_8): δ 8.01 (dd, J = 7.5, 1.4 Hz, 2H, Ar H), 7.69 (d, J = 6.0 Hz, 1H, H(6)), 7.62 (dd, J = 11.0, 6.0 Hz, 1H, H(4)), 7.39 (m, 3H, Ar H), 7.08 (d, J = 11.0 Hz, 1H, H(3)), 6.35 (t, J = 6.0 Hz, 1H, H(5)). ^{11}B NMR (160.4 MHz, CDCl$_3$): δ 39.6. ^{13}C NMR (125.7 MHz, c-C$_6$D$_{12}$): δ 150.0 (C(6)), 147.7 (C(4)), 134.6 (C$_o$), 131.6 (C$_p$), 128.8 (C$_m$), 125.8 (br, C(3)), 112.5 (C(5)). HRMS (EI; m/z): calcd for $C_{10}H_9{}^{11}BO$, 156.0746 (M$^+$); found, 156.0753. Anal. Calcd for $C_{10}H_9BO$: C, 77.00; H, 5.82. Found: C, 76.97; H, 5.96. **1b**-*d*: When the above reaction was performed using methylene chloride-d_2, the isolated product had a deuterium atom at C(3), as shown by the ^{1}H NMR: no signal at δ 7.08 (H(3)), δ 7.62 signal now d (J = 6.0 Hz, H(4)), the rest of the spectrum unchanged. **9**: A THF (3 mL) solution of **1b** (62.6 mg, 0.40 mmol) was added to Cr(CO)$_3$(CH$_3$CN)$_3$ (104 mg, 0.40 mmol). The resulting red solution was heated to 70 °C for 12 h. After removal of the solvent the crude product was extracted with hexanes to give a bright yellow solution. The solvent was removed, leaving a crystalline product (117 mg). The product was recrystallized from ether/hexanes to give yellow crystals. Mp: 116 °C. IR (hexane, film; cm^{-1}): 1981, 1916. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.68 (dd, J = 11.2, 6.2 Hz, 1H, H(4)), 7.62 (d, J = 4.4 Hz, 1H, H(6)), 6.82 (d, J = 11.2 Hz, 1H, H(3)),6.40 (dd, J = 6.2, 4.4 Hz, 1H, H(5)), 5.96 (d, J = 6.4 Hz, 2H, Ph H), 5.61 (t, J = 6.4 Hz, 1H, Ph H), 5.30 (t, J = 6.4 Hz, 2H, Ph H). ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 233.0, 148.9, 147.8, 124 (br), 112.2, 99.3, 95.6, 91.4. ^{11}B NMR (160.4 MHz, CDCl$_3$): δ 46.5. HRMS (EI; m/z): calcd for $C_{13}H_9{}^{11}BCrO_4$ (M$^+$), 291.9987; found, 291.9999. Anal. Calcd for $C_{13}H_9BCrO_4$: C, 53.47; H, 3.11. Found: C, 53.37; H, 3.03.

(13) For a similar mechanistic proposal see: Nakadaira, Y.; Sato, R.; Sakurai, H. *Organometallics* **1991**, *10*, 435.

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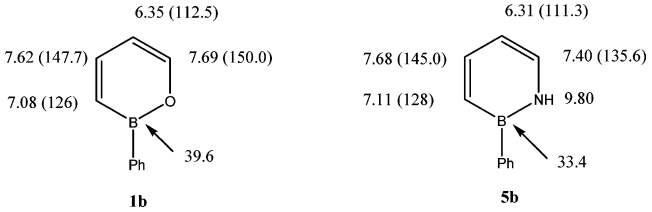
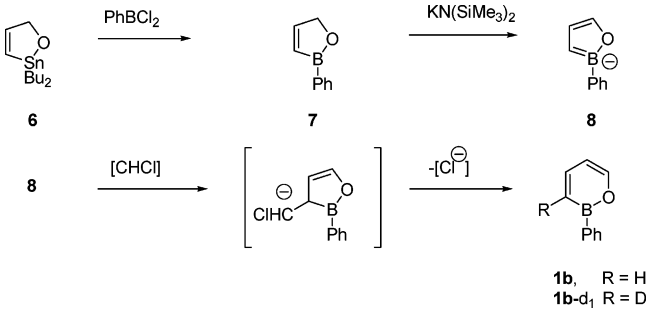
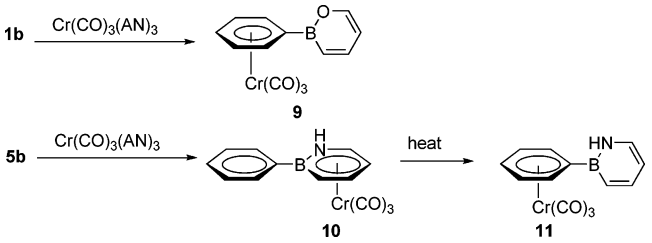


Figure 1. Comparison of the ^{1}H NMR, ^{13}C NMR (in parentheses), and ^{11}B NMR (arrows) chemical shift values of **1b** and **5b** in THF-d_8.

Scheme 1



Scheme 2



^{11}B, and ^{13}C NMR chemical shift values of **1b** are very similar to those of **5b**,[14] as illustrated in Figure 1. There are only small differences in chemical shift values of the atoms near oxygen/nitrogen, which are consistent with the different electronegativities of those atoms. Overall the similarity of the spectra is consistent with a similarity in electronic structure of the two compounds. In this context it is important to emphasize that 1,2-dihydro-1,2-azaborine (**5a**) has classical aromatic properties.[15]

The reaction of **1b** with $Cr(CO)_3(CH_3CN)_3$ in THF at 70 °C gave yellow crystals of **9** (Scheme 2). The molecular structure of **9**,[16] illustrated in Figure 2, resembles that of **11**, the phenyl−$Cr(CO)_3$ complex of **5b**.[17] Apparently the 1,2-dihydro-1,2-oxaborine ring is a poorer ligand than phenyl. Interestingly, the corresponding reaction of **5b** with $Cr(CO)_3(CH_3CN)_3$ initially forms **10**. Compound **10** is only converted to the phenyl-coordinated **11** on subsequent heating.[17] The uncoordinated 1,2-oxaborine ring of **9** is completely planar (±0.004 Å) and is canted by 5.7° relative to the phenyl ring. The intra-ring bond distances of the oxaborine ring are close to those calculated by DFT for **1a** (average difference, 0.02 Å). It is particularly noteworthy that the endocyclic B−C bond (1.481(8) Å) is

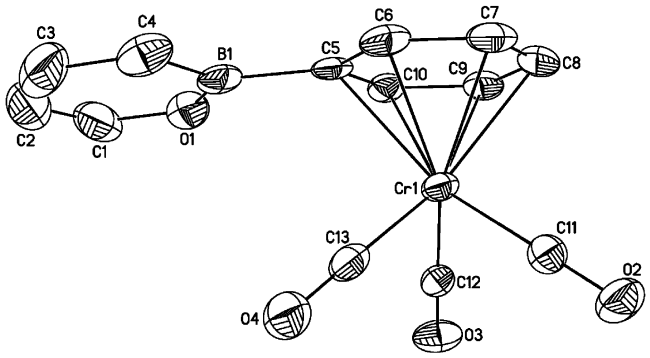
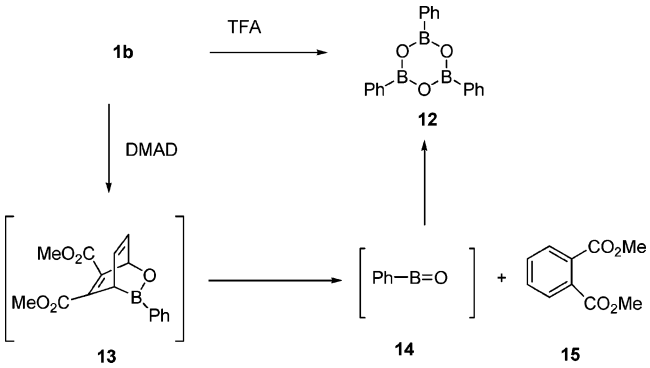


Figure 2. Solid-state structure of **9** (ORTEP). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å): B(1)−C(5), 1.567(7); B(1)−C(4), 1.481(8); C(4)−C(3), 1.391(8); C(3)−C(2), 1.433(9); C(2)−C(1), 1.308(9); C(1)−O(1), 1.359(7); O(1)−B(1), 1.384(6).

Scheme 3



significantly shorter than the exocyclic B−C bond (1.567(7) Å). Thus, the structural data for **9** are consistent with a delocalized π-bonding in the 1,2-dihydro-1,2-oxaborine ring.

In order to explore possible electrophilic hydrogen/deuterium exchange, **1b** was treated with CD_3CO_2D/CF_3CO_2D at 25 °C. This reaction led only to the formation of phenylboronic anhydride **12** and other unidentified products. Under identical conditions treatment of **5a** with CF_3CO_2D led to H/D exchange. The reaction of **1b** with dimethyl acetylenedicarboxylate (DMAD) in benzene at 90 °C gave **12** and dimethyl phthalate (**15**)**.** These products are probably formed via a Diels−Alder reaction to give **13**,[18] followed by an Alder−Rickert cleavage, as illustrated in Scheme 3. Phenyloxyborane (**14**) may be the precursor of **12**.[19] Under identical conditions **5** and DMAD do not react.

In summary, we have developed a new synthesis which allows the preparation of a minimally substituted 1,2-dihydro-1,2-oxaborine. Preliminary investigation of the chemistry of **1b** reveals that the 1,2-dihydro-1,2-oxaborine ring is readily cleaved under mild conditions. However, the molecular structure of **9** suggests that the 1,2-dihydro-1,2-oxaborine ring is aromatic, as had been predicted by DFT calculations.

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Supporting Information Available: A CIF file giving crystallographic data for **9**. This material is available free of charge via the Internet at http:pubs.acs.org.

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(14) Pan, J.; Kampf, J. W.; Ashe, A. J., III. *Organometallics* **2004**, *23*, 5626.

(15) Pan, J.; Kampf, J. W.; Ashe, A. J., III. *Org. Lett.* **2007**, *9*, 679.

(16) Crystal data for **9**: $C_{13}H_9BCrO_4$, monoclinic, $P2_1/c$, a = 11.672(2) Å, b = 7.113(1) Å, c = 15.635(2) Å, β = 107.503(8)°, V = 1238.0(3) Å^3, Z = 4, D_c = 1.567 g cm^{-3}, T = 150(2) K, λ(Mo Kα) = 0.710 73 Å. Data were collected on a Siemans SMART CCD instrument. Final R indices ($I > 2\sigma(I)$): R1 = 0.0606, wR2 = 0.1292. R indices (all data): R1 = 0.1122, wR2 = 0.1408. GOF on F^2 = 1.088.

(17) Pan, J.; Kampf, J. W.; Ashe, A. J., III. *Organometallics* **2006**, *25*, 197.

(18) Heating **1b** with DMAD in benzene-d_6 to 65 °C for 16 h resulted in partial conversion to **12** and **15**. However, no intermediate products were detected by ^{1}H NMR spectroscopy.

(19) See: Pachaly, B.; West, R. *J. Am. Chem. Soc.* **1985**, *107*, 2987.