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Notes

1,5-Bis(dimethylamino)dibenzo[*b,f*]-1,5-diborocane from the Dehalogenation of Dichloro(2-((dimethylamino)methyl)phenyl-*C,N*)boron

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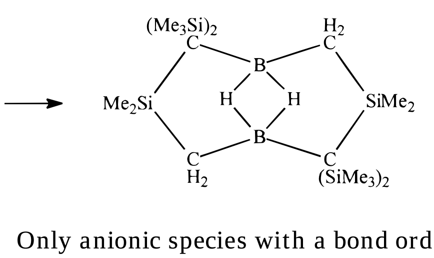
*Summary: The reduction of dichloro(2-((dimethylamino)methyl)phenyl-C,N)boron (**1**) with sodium results in the formation of 1,5-bis(dimethylamino)dibenzo[b,f]-1,5-diborocane (**2**). An internal donor stabilization of a presumptive (BB) double bond between two boron atoms with organyl substituents was not achieved.*

Introduction

It is well known that moieties which are not stable thermodynamically can be stabilized kinetically by bulky substituents. This concept has been used to prepare and isolate many species having double bonds between elements of the third, fourth, and fifth row of the periodic table. For example, see review[1] for the elements Si, Ge, and Sn.

This concept, however, has its limits when the desired structures are thermodynamically too far from stability.[2] This is the case apparently if a double bond between two organyl-substituted boron atoms is the aim.[3] In this case the reactivity of the intermediate is so high that an intramolecular reaction leads to a product of distinct thermodynamic stability. This is exemplified in eq 1.[3]

$$2\,(Me_3Si)_3C\text{—}BCl_2 \xrightarrow[-\,4\,(Na/K)Cl]{+\,4\,Na/K} \left[\,(Me_3Si)_3C\text{—}B{=}B\text{—}C(SiMe_3)_3\,\right]$$

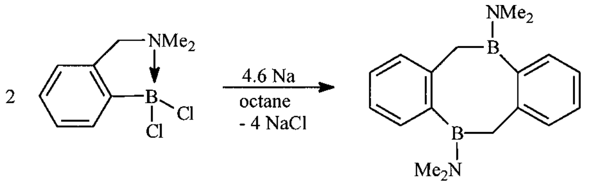


(1)

Only anionic species with a bond order clearly exceeding one between boron atoms have been isolated so far.[4−6] So it was of interest to see if a (BB) double bond between organyl substituted boron atoms could be stabilized by intramolecular donor stabilization.

Results and Discussion

We chose dichloro(2-((dimethylamino)methyl)phenyl-*C,N*)boron (**1**) as the starting material and dehalogenated it with sodium in octane (eq 2). The crude product thus obtained did not give reactions indicative of unsaturation between the boron atoms. For example, no addition of elemental sulfur or selenium was observed. Finally, the X-ray structure analysis of the purified product showed that 1,5-bis(dimethylamino)dibenzo[*b,f*]-1,5-diborocane (**2**), a compound without a B═B bond, was the product that had been formed.



(2)

1 **2**

It is likely that **2** was formed from a dimeric (with respect to **1**) intermediate containing a (BB) bond. Stabilization is achieved by formation of the strong (BN) covalent bonds and of the (CH_2−B) bonds. The only report of the 1,5-diborocane ring system dates back to 1959. The synthesis was achieved by alcoholysis of a polymer obtained from triallylborane and triisobutylborane, and the characterization just meets the requirements of that time.[7] However, 3,7,9,11-tetrakis(dimethylamino)-3,7,9,11-tetraboratricyclo[4.2.2.2^{2,5}]-dodecane, obtained by Herberich et al.[8] by catalytic dimerization of 1,2-bis(dimethylamino)-1,2-dibora-4-cy-

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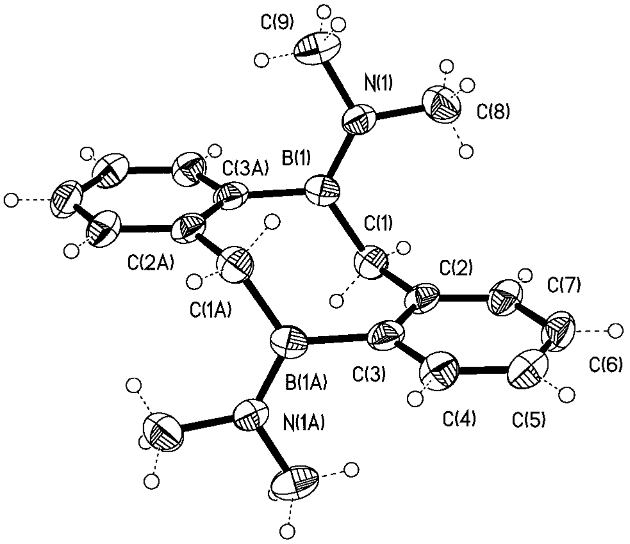

Figure 1. Perspective drawing and numbering scheme for **2** with anisotropic displacement parameters depicting 50% probability. Selected bond distances (mean values) B−N 1.388(6) Å; B−C(3) 1.572(7) Å; B−C(1) 1.592(7) Å; C(1)−C(2) 1.515(6) Å; C(2)−C(3) 1.403(6) Å. Torsion angle (chair conformation) (mean value): C(2)−C(1)−B(1)−C(3A) 108.7(4)°.

clohexene, also contains two 1,5-diboracyclooctane units with common >CH-HC< ring members and was characterized by its X-ray structure. The description of the latter system is that of a dimer of two 1,4-diboracyclohexanes.

Experimental Section

The reactions and manipulations were performed under an inert atmosphere of dry nitrogen. Melting points were determined in sealed capillaries. NMR spectra were recorded in $CDCl_3$ on a Bruker MSL-400 instrument. Mass spectra were obtained on a Finnigan MAT 8230 spectrometer.

Compound 1. A 463 mL amount of a 1.6 M BuLi solution in hexane was added dropwise with stirring to a solution of 100.0 g (0.74 mol) *N*-benzyldimethylamine dissolved in 300 mL of hexane at 20 °C. After refluxing for 3 h, 86.8 g (0.74 mol) of gaseous BCl_3 was passed into the solution at −40 °C. The reaction mixture was brought to ambient temperature overnight. Solid material was filtered and sublimed in high vacuum in a three-bulb apparatus. **1** sublimed at 120 °C/0.001 Torr (air bath temp.) to give 98.0 g of colorless crystals, mp 138 °C (62% yield). Anal. Calcd for $C_9H_{12}BCl_2N$ (215.92): C, 50.07; H, 5.60; Cl, 32.84; N, 6.49. Found: C, 49.06; H, 5.51; Cl, 32.20; N, 6.27. MS: EI *m/e* (rel intensity) 215(12) $[M]^+$, 180(100) $[M - Cl]^+$. ^1H NMR: δ 2.80 (s), 4.20 (s), 7.20 (m, br). ^{13}C NMR: δ 47.5, 67.7, 122.5, 128.4, 128.5, 129.5, 136.7, 145 (br). ^{11}B NMR: δ 10.8.

Compound 2. A suspension of 23.65 g (0.11 mol) of **1** in 350 mL of octane was heated at reflux with stirring with 6.0 g (0.26 mol) of sodium for 6 h. The color of the reaction mixture changed from yellowish to black. Filtration at ambient temperature through a glass frit yielded an orange filtrate. The residue was washed twice with 50 mL of octane and still contained 8.0 g of unreacted **1**. The solvent was evaporated from the filtrate under reduced pressure, and the remaining viscous material was distilled under vacuum in a three-bulb tube. Compound **2** (9.0 g) was collected at 110 °C/0.001 Torr (air bath temperature) as a yellow, honeylike material which upon treatment with 20 mL of hexane gave colorless crystals, mp 60 °C. Taking into account the unreacted starting material, the yield of **2** is 42%. $C_{18}H_{24}B_2N_2$ (290.01). MS: EI (high resolution) Calcd: 290.2132; Found: 290.2143 $[M]^+$; FI *m/e* (rel intensity) 290(100). ^1H NMR: δ 1.23 (s, 4H), 2.38 (s, 12H), 7.1 (m, br, 8H). ^{13}C NMR: δ 30.8, 47.4, 122.4, 128.3, 128.4, 129.6, 137.7, 143 (br). ^{11}B NMR: δ 44 (br).

X-ray Structure Determination of 2. Crystallographic data: $C_{18}H_{24}B_2N_2$, fw = 290.01, monoclinic $P2_1/c$, $a = 17.473(4)$ Å, $b = 7.434(2)$ Å, $c = 13.810(3)$ Å, $\beta = 113.23(3)°$, $V = 1648.5(6)$ Å^3, $Z = 4$, 203(2) K. Full matrix refinement (based on F_o^2, SHELX-93) of the positional and anisotropic displacement parameters for the non-hydrogen atoms converged with $R1 = 0.0804$, $wR_2 = 0.2030$ for 2173 independent reflections with $I > 2\sigma(I)$. Refinement of the two half independent molecules was accomplished by SHELXL-93 using no restraints. Hydrogen atoms were positioned geometrically, and in the case of methyl groups torsion angles were refined. The hydrogen atoms were given 1.5 times the equivalent isotropic U of the connected carbon. Plots have been prepared by XP molecular graphics contained in Siemens SHELXTL. There are two independent half molecules in the asymmetric unit completed by an inversion center, thus the phenyl rings are coplanar. The two completed molecules can be fitted to each other after inversion. The main deviations between the two molecules are seen at the dimethylamino groups, arising from slightly different conformers of the eight-membered ring.

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Supporting Information Available: Tables of crystal data, complete fractional coordinates, anisotropic displacement parameters, bond lengths and angles, and selected torsion angles and a fully labeled figure at the 50% probability level and a plot with a fit of the two conformers of **2** (8 pages). Ordering information is given on any current masthead page.

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