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Compounds of Pentacoordinate (10-B-5) and Hexacoordinate (12-B-6) Hypervalent Boron[1]

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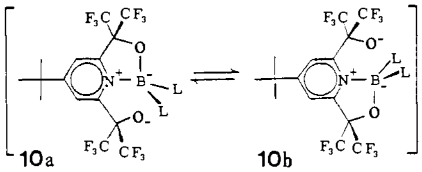
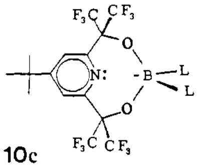
Hypervalent[2] compounds of only two first-row elements, carbon[3] and fluorine,[4] have been reported. Although nucleophilic associative displacement processes, via pentacoordinate (10-B-5)[1] boron transition states,[5] proceed with low activation energies,[5] there is no prior evidence for hypervalent boron ground states. We here report evidence for isolable 10-B-5 and 12-B-6 species.

Dilithio derivative **2** of pyridine diol **1**[6] reacts with BCl_3 to give chloroborate **3** in high yield. Reaction of dilithiobiphenyl-(**4**)[7] with **3** gives the yellow anion of **5**, stable as its crystalline tetraethylammonium salt. Reaction of **3** in tetrahydrofuran (THF) with Grignard reagent **6**[8] at −78 °C, upon addition of Et_4NCl in dioxane (25% of the volume of the THF), gives **7**, a stable white tetraethylammonium salt. Oxidation of **7** with $Ph_3COSO_2CF_3$[9] gives **8**. Chloroborate **3** reacts with dilithio derivative **2** at 110 °C to give, after cation exchange, white crystalline compound **9**.

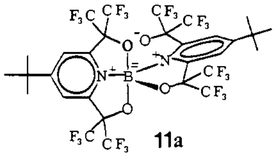
Structures **10a–c**, 8-B-4 alternatives for 10-B-5 structures **5**, **7**, and **8**, are related to these preferred structures by B–O or B–N bond heterolysis. Structures **11a–c** must be considered as alternatives for 12-B-6 species **9**.



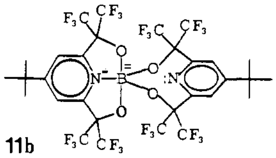
10a 10b



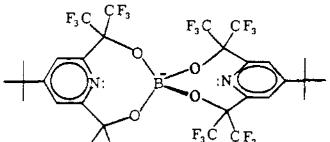
10c



11a

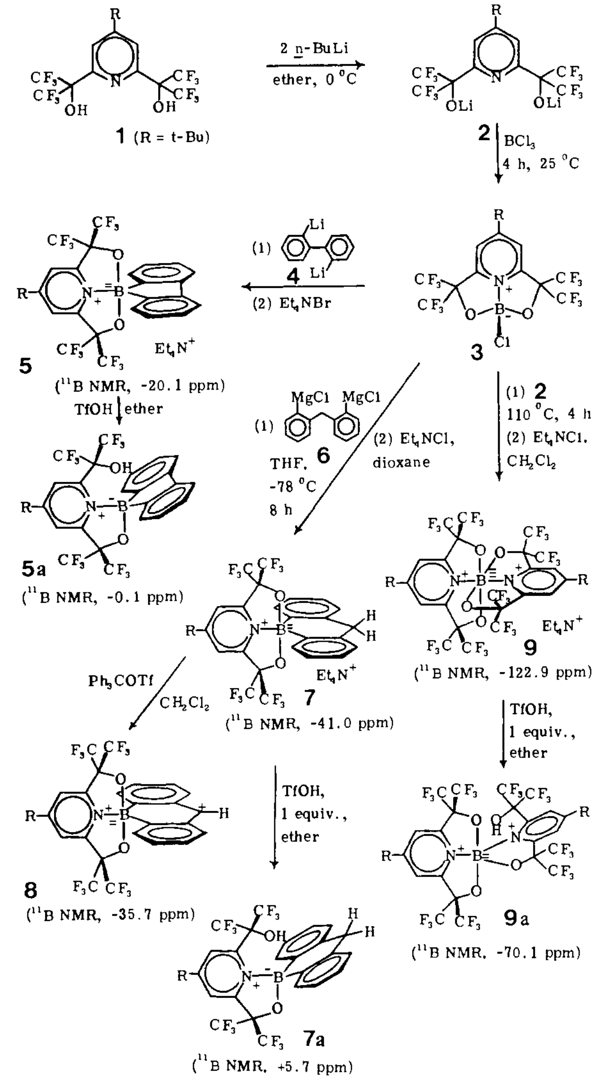


11b



11c

Scheme I



The ^1H NMR spectra of **5**, **7**, **8**, and **9** show only one singlet for the pyridine 3- and 5-protons,[10] 0.20–0.23 ppm downfield from that of the analogous protons in diol **1** (7.90 ppm) and 0.10–0.13 ppm downfield from that of chloroborate **3** (7.97 ppm), compatible with the N–B coordination in **5**, **7**, **8**, and **9**. The ^{13}C NMR spectra[10] are also consistent with symmetrical structures for **5**, **7**, and **9**. The ^{19}F NMR spectra of compounds **5**, **7**, **8**, and **9** (at 338.76 MHz) each show only one sharp singlet over the temperature range 25 to −105 °C.[11] While consistent with symmetrical structure **5**, **7**, **8**, and **9**, this does not rigorously rule out rapidly equilibrating unsymmetrical structures such as **10a** and **10b** or **11a** and **11b**.

The high-energy barriers usually seen for conformational averaging processes in eight-membered ring species, such as **10c**, are well-known.[12] Structures **10c**, **11b**, and **11c**, without the N–B bond, are [5]metacyclophanes, expected to show high barriers to

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(9) The published preparation method (Forbus, T. R.; Martin, J. C. *J. Org. Chem.* **1979**, *44*, 313) was modified by using pentane as solvent and the isolated yield of trityl triflate was quantitative.

(10) ^1H NMR ($CDCl_3$) single peaks for the pyridine 3- and 5-protons of **1**, **3**, **7**, **8**, and **9** are found at δ 7.90, 7.97, 8.20, 8.15, 8.19, and 8.16 respectively. ^{13}C NMR (CD_2Cl_2): **5**, δ 8.22, 30.39, 34.04, 53.60, 78.18, 100.03, 122.16, 122.38, 128.69, 130.61, 139.53, 149.64, 165.57. **7**, δ 7.94, 30.39, 35.99, 52.96, 80.44, 99.55, 121.55, 122.12, 127.94, 129.34, 129.88, 138.80, 147.21, 148.34, 148.80, 164.70. **9**, δ 8.06, 30.11, 53.35, 80.41, 122.40, 126.14, 139.98, 157.44.

(11) The ^{19}F NMR chemical shifts (338.76 MHz) at 25 °C for **5**, **7**, **8**, and **9** are δ −75.30 (s), −73.65 (s), −73.89 (s), and −74.71 (s), respectively. The spectra are unchanged (within 0.2 ppm) at −105 °C.

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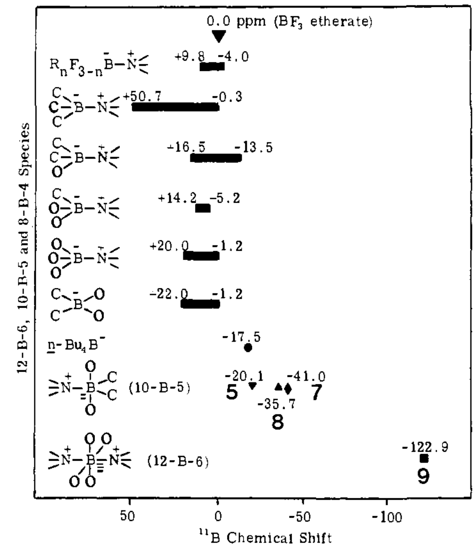
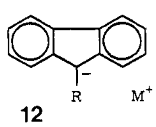


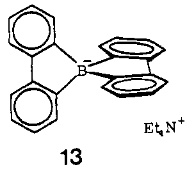
Figure 1. Ranges of ^{11}B NMR chemical shifts reported[18] for 8-B-4 borates, with first-row elements C, N, O, and F attached to boron, compared with the chemical shifts of 10-B-5 species **5**, **7**, and **8** and 12-B-6 species **9**.

inversion,[13] with nonequivalent geminal CF$_3$ groups, if the interaction between the nitrogen and boron were repulsive. The 8-B-4 borate anion o **10c** acts as a Lewis acid toward the transannular pyridine nitrogen to give the more stable ring-closed product **5**.[14]

The electronic spectrum of yellow 10-B-5 species **5** (λ_{max} = 397 nm, ϵ 1650)[15] is consistent with delocalization of electrons of the hypervalent three-center, four-electron O-B-O bond into π-acceptor diequatorial five-membered ring, making it a bis-ipso aromatic[3a] 6-π Hückel aromatic system analogous to yellow fluorenyl anion **12**.[16] Spirobicyclic borate **13**,[17] is, in contrast, colorless.



12



13

The reported ^{11}B NMR chemical shifts for 8-B-4 species with only first-row elements (F, O, N, C) attached to the quaternary borons are downfield of −17.5 ppm.[18] The observed ^{11}B NMR chemical shifts for **5**, **7**, and **8** are upfield of this, at −20.1, −41.0, and −35.7 ppm, respectively. That for 12-B-6 species **9** is −122.9 ppm, about 80 ppm upfield of 10-B-5 species **5**, **7**, and **8** and ca. 130 ppm[18] upfield of ordinary 8-B-4 compounds. This strongly supports the postulated, unprecedented 12-B-6 structure for **9**.

Compounds **5**, **7**, and **9** react with triflic acid (TfOH) to give colorless solutions whose ^{11}B NMR spectra show signals in the range associated with 8-B-4 species such as **5a** and **7a** in Figure 1. Both **5a** and **7a** show ^{19}F NMR peaks for nonequivalent CF$_3$ groups at room temperature. The monoprotonation of **9** gives **9a**, a 10-B-5 species with a chemical shift (−70.1 ppm) near those of the other 10-B-5 species **5**, **7**, and **8**.

The above evidence strongly supports our conclusion that these are the first hypervalent boron compounds, 10-B-5 and 12-B-6 species.[19-21]

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[14] The conversion of **10c** to **5** is expected[2e] to result in negative charge delocalization onto both oxygens.

[15] Follows Beer's law—extinction coefficient constant after three recrystallizations.

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[19] Compounds **3**, **5**, **7**, **8**, and **9** showed molecular ions in their mass spectra. All except **8** gave satisfactory elemental analyses.

[20] The 8-B-5 and 8-B-6 borons in carboranes[21] are electron deficient and only superficially similar to the 10-B-5 and 10-B-6 species reported here.

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Syntheses of Heme *d* Models

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A gradually increasing number of biological redox systems have recently been shown to possess hydroporphyrin hemes (iron chlorins) as their prosthetic groups. Examples include siroheme,[1] probably the heme in hemoglobin[2] and the prosthetic group in myeloperoxidase,[3] as well as the green hemes (originally called heme a_2, now called heme d),[4] from *Escherichia coli* and other bacteria, various cd-type nitrite reductases,[5-9] and the catalase from *Neurospora crassa*.[10,11] Barrett[4] showed the heme d from *Aerobacter aerogenes* and *Escherichia coli* to be related to protoporphyrin IX and, as a result of various classical chemical and spectroscopic studies, suggested several structures similar to **1** for heme d; all had vinyl, ethyl, or hydroxyethyl groups at C-2 and C-4, and though the site of subunit reduction was not defined, it has since been generally assumed to be ring D;[12] this assumption presumably arose because all known chlorophyll derivatives are reduced in that ring. The green heme from the *Neurospora crassa* catalase appears[11] to have four (rather than two) carboxylate groups and cannot be reoxidized to a porphyrin using high-potential quinones.

In this paper we describe a route, from chlorophyll a, for the synthesis of the heme d model **2**, which is structurally analogous to Barrett's heme d, and then develop a procedure for synthesis and separation of all possible ring-reduced isomers of this compound. A logical synthetic approach to a pigment such as **2** would be from natural chlorophyll derivatives, and the problem resolves itself into the "retro-biosynthetic"[13] conversion of the isocyclic (ring

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