

Subporphyrinato Boron(III) Hydrides

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S Supporting Information

ABSTRACT: Subporphyrinato boron(III) hydrides were prepared by reduction of subporphyrinato boron(III) methoxides with diisobutylaluminum hydride (DIBAL-H) in good yields. The authenticity of the B–H bond has been unambiguously confirmed by a ¹H NMR signal that appears as a broad quartet at –2.27 ppm with a large coupling constant with the central ¹¹B, characteristic B–H infrared stretching frequencies, and single crystal X-ray diffraction analysis. Red shifts in the corresponding absorption and fluorescence profiles are accounted for in terms of the electron-donating nature of the B-hydride. The hydridic character of subporphyrinato boron(III) hydrides has been demonstrated by the production of H₂ via reaction with water or HCl, and controlled reductions of aromatic aldehydes and imines in the presence of a catalytic amount of Ph₃C[B(C₆F₅)₄].

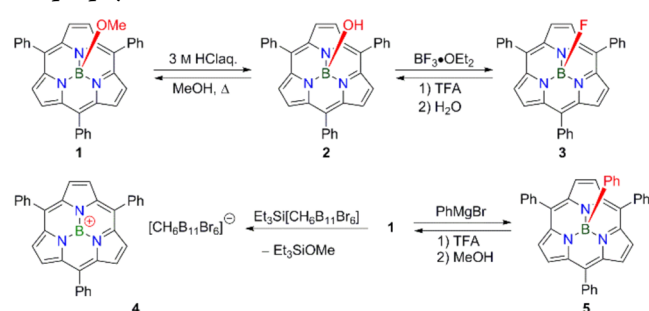
In recent years, subporphyrin, a ring-contracted 14 π -porphyrin cousin consisting of three pyrrole units connected via three methine carbon atoms, has emerged as a new class of functional pigments.^{1–4} While subporphyrins and porphyrins share many common attributes such as strong absorption, fluorescence, and aromaticity, the former bears an axial B-substituent that can be used for fine-tuning the overall reactivities and electronic properties. Different from subphthalocyanines, a ring-contracted 14 π -phthalocyanine cousin,^{1,5} the axial substituent of subporphyrin can be readily exchanged as depicted in Scheme 1. Subporphyrinato boron(III) methoxide (hereinafter referred to as subporphyrin B-methoxide) **1** can be quantitatively converted into subporphyrin B-hydroxide **2** upon treatment with an aqueous HCl solution, while heating **2** in the presence of an

excess amount of methanol regenerates **1**.^{2a,b,4} Subporphyrin **2** can be converted to subporphyrin B-fluoride **3** upon treatment with an excess amount of BF₃·OEt₂.^{4c} Furthermore, B-arylated subporphyrin **5** can be prepared from the reaction of **1** with the appropriate Grignard reagent,^{4e} and subporphyrin borenium cation **4** can be isolated as a stable salt with a noncoordinating carborane counteranion.^{4d}

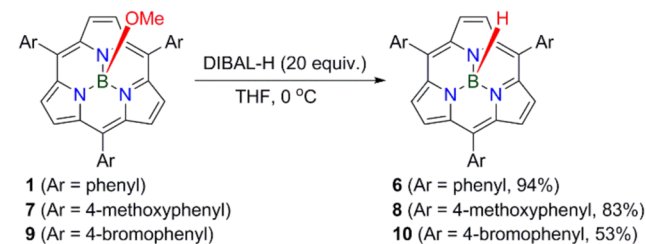
Subporphyrin B-hydride is a new and promising variant that may be utilized as a reducing reagent or may possess interesting properties. However, due to the difficulty of preparation, examples of B-hydrides of porphyrinoids have remained elusive in the literature thus far. While a considerable body of work by Brothers et al. documents the synthesis and reactivity of boron porphyrins,^{6a,b} a diboron-coordinated corrole was reported as the sole example of such a species.^{6c} In this paper, we disclose the first synthesis of subporphyrin B-hydrides.

Initial attempts to synthesize subporphyrin B-hydride **6** involved reactions of **1** with various hydride reducing agents. While **1** was unreactive toward NaBH₄, even in refluxing THF, treatment of **1** with LiAlH₄ at 0 °C resulted in over-reduction to give a complex mixture, from which it was possible to isolate a trace amount of **6**. The yield of hydride transfer was increased to 20% when using LiAlH₄ in a 1:1 mixture of THF/CH₂Cl₂. Finally, we found that DIBAL-H was the optimum hydride delivery reagent, as **6** was produced in 94% yield when the reduction was performed with 20 equiv of DIBAL-H in THF at 0 °C followed by quick separation over a neutral alumina column and subsequent recrystallization (Scheme 2). Under similar conditions, subporphyrin B-hydrides **8** and **10** were synthesized from **7** and **9** in 83% and 53% yields, respectively. The Lewis acidic nature of DIBAL-H is likely important in these reductions by facilitating liberation of the B-methoxy group from **1** (see Supporting Information, SI, for a possible reaction mechanism).

Scheme 1. Axial-Ligand Exchange Reactions of Subporphyrins



Scheme 2. Synthesis of Subporphyrin B-Hydrides



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Scheme S10). The importance of employing a Lewis acidic hydride source was confirmed by reduction of **1** with AlH_3 generated from LiAlH_4 and AlCl_3 ,⁷ which gave **6** in 76% yield. This method was used for preparation of subporphyrin B-deuteride **6-D** in 74% yield.

High resolution atmospheric pressure chemical ionization-time-of-flight mass spectroscopy (HR-APCI-TOF-MS) operating in negative ion mode revealed the parent anion peak of **6** at $m/z = 471.1920$ (calculated for $[\text{C}_{33}\text{H}_{22}^{11}\text{BN}_3]^- = 471.1918$) with an isotopic distribution consistent with the chemical composition. In the ^1H NMR spectrum of **6** in CDCl_3 , the B-hydride signal was observed as a broad quartet at -2.27 ppm with $^1J_{\text{BH}} = 152$ Hz ($^{11}\text{B}-^1\text{H}$ coupling) at 60°C .⁸ Upon decreasing temperature the quartet signal gradually coalesced to a broad singlet signal due to rapid quadrupole-induced spin relaxation at lower temperature.⁹ In the ^{11}B -decoupled ^1H NMR spectrum of **6**, the B-hydride signal was observed as a singlet and the ^1H NMR spectrum of **6-D** is identical to that of **6** except for the absence of the B-hydride signal. The ^1H NMR chemical shifts have been calculated by density functional theory (DFT) using the gauge-including atomic orbital (GIAO)¹⁰ method at the B3LYP/6-31G(d) level,¹¹ which predicts the chemical shift of the B-hydride of **6** to reside at -2.40 ppm which is consistent with the experimental value. The ^{11}B NMR spectrum of **6** in CDCl_3 showed a broad doublet at -19.7 ppm with $^1J_{\text{HB}} = 147$ Hz at rt.⁸ When comparing the respective ^{11}B chemical shifts of compounds **1** (-15.1 ppm), **2** (-15.6 ppm), **3** (-14.8 ppm), and **5** (-16.4 ppm), compound **6** indicates that an axial hydride is the most electron-donating among these axial substituents. The infrared spectra of **6** and **6-D** display B-H and B-D stretching vibrations at 2280 and 2186 cm^{-1} , and 1716 and 1690 cm^{-1} , respectively, which are smaller than those of the corresponding reported matrix isolated BH_3NH_3 (2427 and 2417 cm^{-1}) and BD_3ND_3 (1837 and 1817 cm^{-1}).¹² These results suggest weaker B-H and B-D bonds on **6** and **6-D** than the corresponding ammoniaboranes.

Structural confirmations of **6**, **8**, and **10** have been revealed by X-ray diffraction analyses of their single crystals.¹³ The crystal structure of **6** contains two independent but similar bowl-shaped molecules in the unit cell, and one of them is indicated in Figure 1a. The bowl-depths, defined by the distance between the boron atom and the mean plane of the six peripheral β -carbons, are 1.353 and 1.344 Å, and the B-N bond lengths of **6** are in the range of 1.495 – 1.505 Å. These structural features are quite

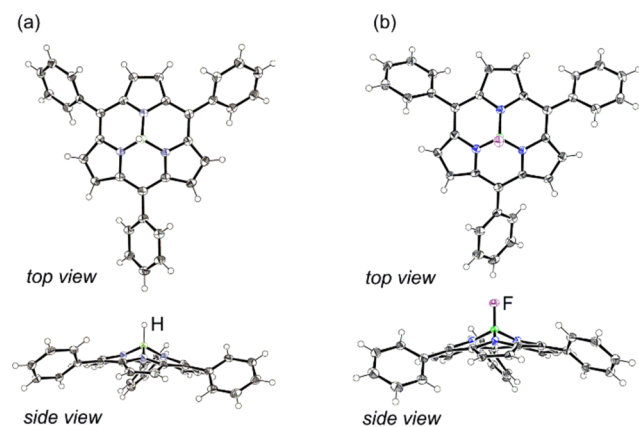


Figure 1. X-ray crystal structures of **6** (a) and **3** (b). Thermal ellipsoids are scaled to 50% probability. Solvent molecules are omitted for clarity.

similar to those of **1**, thus indicating that the central B atom of **6** is sp^3 hybridized similarly to **1**. The crystal structures of **8** and **10** also reveal similar bowl-shaped structures. Importantly, the B-H has been confirmed by refinement of X-ray diffraction data owing to its electron-rich hydride character, which has allowed us to determine the B-H bond lengths to be $1.257(19)$ and $1.21(2)$ Å for **6** and $1.266(15)$ Å for **8**, being slightly longer than those of a previously reported standard ammoniaborane complex ($1.15(3)$ and $1.18(3)$ Å).¹⁴ These results indicate weaker B-H bonds of **6** and **8** compared to the ammoniaborane complex, consistent with the infrared analyses. In the course of this study, we have succeeded in the structural determination of subporphyrin B-fluoride **3**,¹³ which was reported by Kobayashi et al. in 2009,^{4c} but its solid state structure has remained elusive. The crystal structure of **3** contains two independent subporphyrin molecules in the unit cell. The bowl-depths are 1.294 and 1.305 Å, and the B-F bond lengths are $1.412(4)$ and $1.409(4)$ Å, which are comparable to those of dipyrromethene-coordinated difluoroboron complexes (1.39 – 1.40 Å).¹⁵

The Soret-like and Q-like bands of **6** are observed at 387 and 512 nm, with the fluorescence profile peaking at 560 nm with an absolute fluorescence quantum yield of 0.13 . Figure 2a shows the

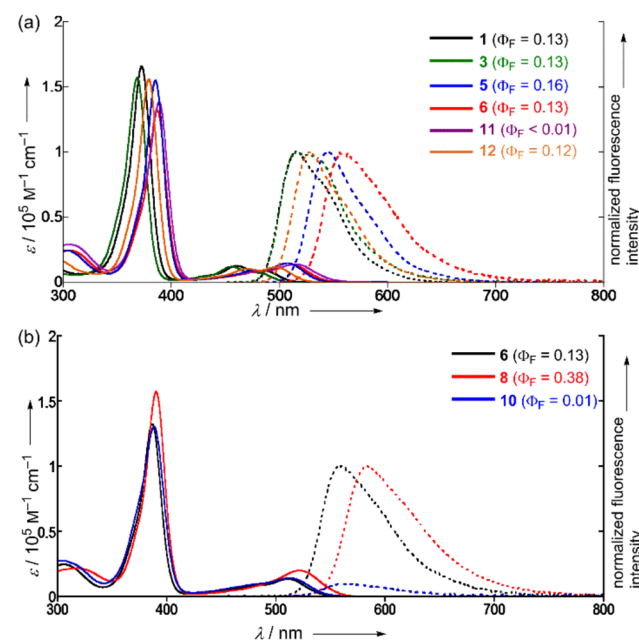


Figure 2. UV-vis absorption (solid lines) and fluorescence (dashed lines) spectra in CH_2Cl_2 . Fluorescence spectra were recorded upon excitation at the peak maxima of each Soret-like bands.

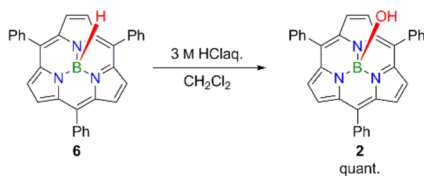
absorption and fluorescence spectra of **1**, **3**, **5**, B-ethyl substituted subporphyrin **11**,^{4e} and B-phenylethynyl substituted subporphyrin **12**.^{4e} Both the Soret-like and Q-like bands are red-shifted in the order $3 < 1 < 12 < 5 < 6 < 11$, reflecting the increasing electron-donating abilities of the axial B-substituents. The fluorescence peaks are red-shifted similarly in the order $3 \leq 1 < 12 < 5 < 6 < 11$. In line with these results, a plot of S_0 – S_1 excitation energies versus Hammett inductive constants σ_I ¹⁷ of the axial B-substituents constitutes a good straight line fit (SI, Figure S4-2). Interestingly, the absorption spectrum of **8** exhibits an enhanced and red-shifted Soret-like and Q-like bands as compared with **6**, probably due to possible intramolecular charge transfer interaction. The fluorescence spectrum of **8** was observed at 583 nm with a quantum yield of 0.38 . While

subporphyrin **6** displayed an absorption spectrum that was very similar to that of **6**, its fluorescence spectrum was observed at 559 nm with a small fluorescence quantum yield ($\Phi_F = 0.01$), apparently due to the effective intramolecular heavy atom effect of the bromine substituents. The fluorescence decay profiles of **6** and **6-D** measured by time-correlated single photon counting techniques were well-fitted with a single exponential function with time constants of 2.9 and 3.1 ns, respectively, which is quite similar to that of **1** ($\tau = 2.95$ ns)^{2b} and slightly larger than that of **5** ($\tau = 2.44$ ns).^{4c}

The oxidation and reduction potentials of **6** were measured by cyclic voltammetry along with those of **1**, **3**, and **5**. The first oxidation of **6** was observed as an irreversible wave at 0.36 V, being lower than the values seen for **1** (0.75 V), **3** (0.84 V), and **5** (0.58 V), again reflecting the electron-donating power of the B-hydride. In contrast, the first reduction potentials did not show significant differences: -1.95 V for **1**; -1.93 V for **3**; -2.01 V for **5**; -1.96 V for **6**. The DFT calculations indicated that only the a_1 symmetric HOMO has large electron coefficients at the boron center, and HOMO-1 and LUMOs have a node at the boron center (SI, Figure S9).¹⁷ These frontier orbital features suggest that changes of the axial B-substituents alter the energy level of HOMO while the energy levels of the other frontier orbitals are left unchanged. Namely, the attachment of an electron-donating B-substituent lifts the energy level of the HOMO and decreases the HOMO-LUMO gap. These theoretical predictions are nicely consistent with the experimental photophysical and electrochemical spectroscopic observations.

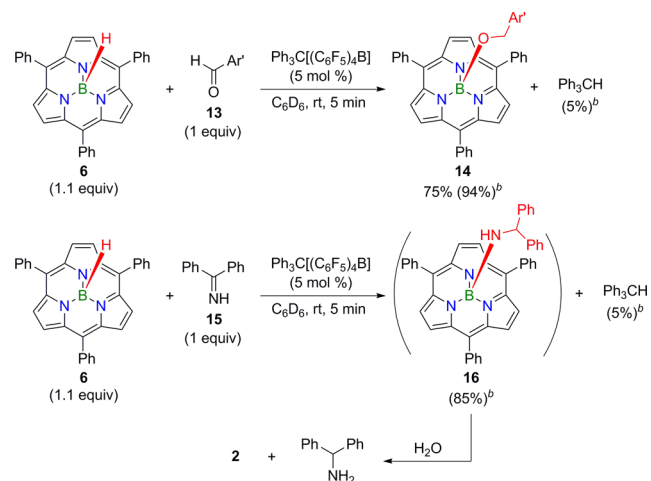
Finally, the chemical reactivity of **6** was studied. Subporphyrin **6** was gradually hydrolyzed to **2** via reaction with adventitious water with concomitant formation of molecular hydrogen gas, as observed by ¹H NMR spectroscopy (SI, Figure S3-5). The hydrolysis rapidly proceeded by washing with an aqueous HCl solution (Scheme 3). However, in the solid state under a nitrogen atmosphere, **6** is stable and storable over several weeks without change.

Scheme 3. Hydrolysis of **6**



In the next step, hydroborations of aldehyde and imine with **6** were examined. The reaction of 3,5-di-*tert*-butylbenzaldehyde (**13**) with **6** (1.1 equiv) in C₆D₆ at rt was very slow, giving only a trace amount of the desired product **14** forming after 24 h (Scheme 4). Interestingly, the reaction was dramatically accelerated and completed in 5 min in the presence of 5 mol % of Ph₃C[(C₆F₅)₄B] to give **14** in 94% yield along with Ph₃CH in 5% yield (¹H NMR yields) (Scheme 4). Product **14** was actually isolated in 75% yield through separation over a short silica gel column, and its structure was confirmed by X-ray diffraction analysis (Figure 3). Similarly, the reaction of benzophenone imine (**15**) with **6** in C₆D₆ gave subporphyrin B-(diphenylmethyl)amide **16**. The ¹H NMR spectrum of the reaction mixture revealed two doublets at -2.36 and 2.44 ppm (by ³J_{HH} = 6.12 Hz) due to the amine and methylene protons of **16** (SI, Figure S3-20). The large high-field shifts of these protons are likely due to the close proximity of the diatropic ring current

Scheme 4. Hydroboration of Arylaldehyde and Imine with **6**^a



^aAr' = 3,5-di-*tert*-butylphenyl. ^bYields in parentheses were determined by ¹H NMR spectroscopy using C₂H₂Cl₄ as an internal standard.

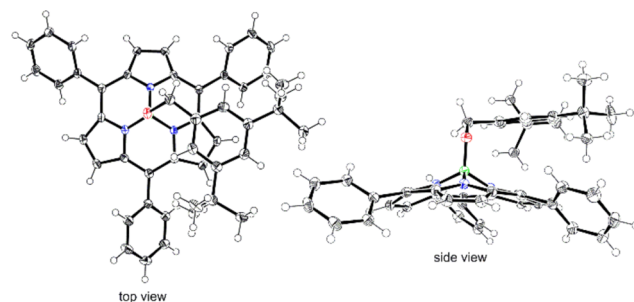
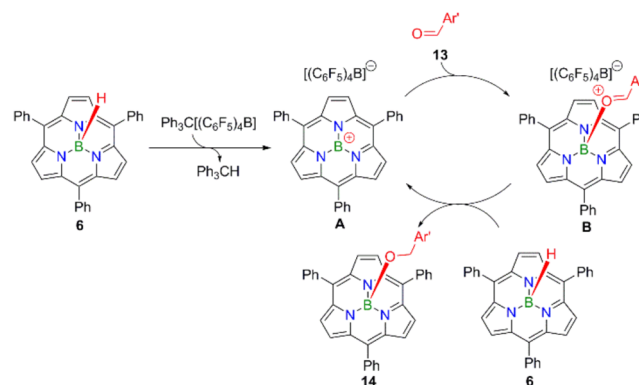


Figure 3. X-ray crystal structure of **14**. Thermal ellipsoids are scaled to 50% probability. Solvent molecules are omitted for clarity.

of the subporphyrin core. In addition, the ¹¹B NMR spectrum of **16** displayed a broad signal at -16.1 ppm coupled with the amine protons. Importantly, product **16** is the first example of subporphyrins bearing an axial B-N bond. Unfortunately, however, all attempts to isolate **16** were unsuccessful so far due to its extremely high hydrolytic reactivity.

A plausible reaction mechanism for the reduction of benzaldehyde with **6** is shown in Scheme 5. The reaction is initiated by abstraction of the hydride of **6** by the trityl cation to generate subporphyrin borenium cation **A**, which activates

Scheme 5. A Plausible Reaction Mechanism for Lewis Acid Catalyzed Hydroboration of Arylaldehyde with **6**



aldehyde **13** to form cationic intermediate **B**. Subsequent hydride transfer from **6** to **B** gives product **14** with reproduction of **A**. The initiation step was actually confirmed by reaction of **6** with a stoichiometric amount of $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 , which led to the quantitative formation of subporphyrin borenium cation tetrakis(pentafluorophenyl)borate salt and Ph_3CH (SI, Figure S3–22). A similar reaction involving a borenium cation as a reaction intermediate for imine hydroboration has been recently revealed by Crudden et al.¹⁸

In summary, the subporphyrin B-hydrides **6**, **8**, and **10** were prepared for the first time by the reduction of subporphyrin B-methoxides **1**, **7**, and **9** with DIBAL-H and were fully characterized. Red shifts in the Soret-like and Q-like bands and fluorescence emission of the subporphyrin B-hydrides are accounted for in terms of the electron-donating nature of the B-hydride that lifts the energy level of the HOMO while leaving other frontier orbitals almost unaffected. The hydridic nature of **6** has been demonstrated by the production of H_2 from the reaction with water or HCl as well as the reductions of aromatic aldehydes and imines in the presence of a catalytic amount of $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$. Study on the exploration of novel reactivities of **6** is worthy of further investigation.

■ ASSOCIATED CONTENT

● Supporting Information

Detailed experimental conditions and procedures, analytical data, theoretical details, and crystallographic data for compounds **8** and **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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