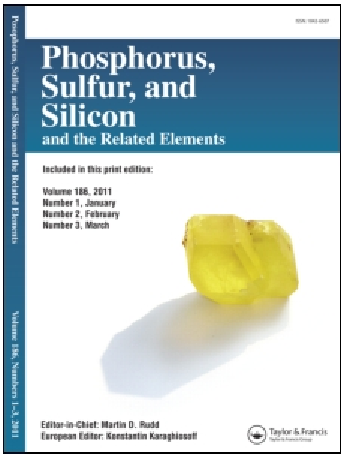

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Synthesis, Optical Properties, and Reactivities of A Dibenzophosphaborin and Its Derivatives

Junji Kobayashi[a]; Tomohiro Agou[a]; Takayuki Kawashima[a]
[a] Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

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Synthesis, Optical Properties, and Reactivities of A Dibenzophosphaborin and Its Derivatives

Junji Kobayashi, Tomohiro Agou, and Takayuki Kawashima
Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

Dibenzo-1,4-phosphaborins were synthesized and characterized by X-ray crystallographic analysis. The phosphaborins exhibited UV/vis absorption derived from intramolecular charge transfer from the phosphorus atom to the boron atom. The phosphaborins showed different fluorescent properties depending on the substituents on the phosphorus atom. The phosphaborin was easily derivatized to P-sulfide, P-selenide and phosphonium salt. The phosphaborin and its P-derivatives formed complexes with fluoride ion. The complex formation constants were shown to increase in accordance with the decrease in their LUMO energy levels.

Keywords Fluorescence; fluoride sensing; heteraborins; hetero-π-conjugated molecules

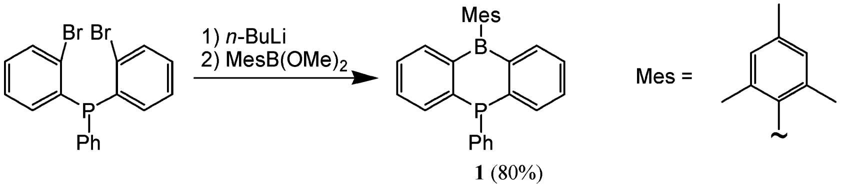
INTRODUCTION

π–Conjugated molecules with novel electronic and optical properties are desirable for constructing organic functional materials including organic semiconductors and light emitting devices. Recently, incorporation of main group elements into π-conjugated systems has been reported as an efficient methodology to decrease HOMO-LUMO energy gaps because of π-conjugation between π-orbitals and donor or acceptor orbitals on main group elements. Among these classes of molecules, boron-containing hetero π-conjugated molecules have attracted much attention because they have a vacant 2p orbital on the boron atom, which can decrease the LUMO level and respond to external stimuli (i.e. Lewis bases). Herein we report the syntheses and the properties of a dibenzophosphaborin and its derivatives as the novel boron-containing hetero π-conjugated molecules.

Address correspondence to Takayuki Kawashima, Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: takayuki@chem.s.u-tokyo.ac.jp

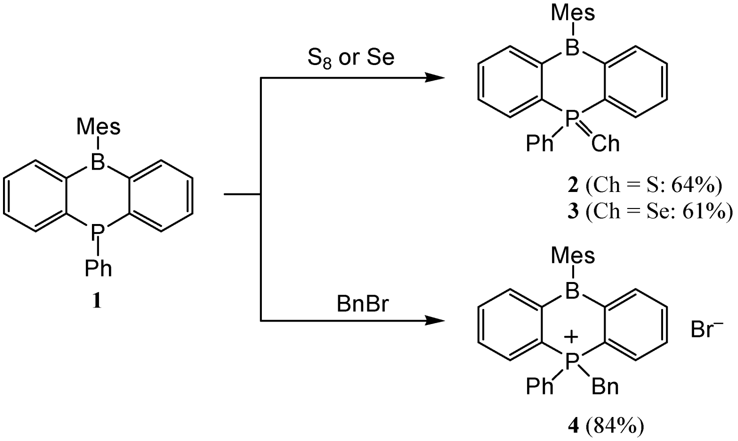
RESULTS AND DISCUSSION

B-Mesityl-*P*-phenylphosphaborin **1** was synthesized by the reaction of dilithio derivative prepared from the bis(2-bromophenyl)phenyphosphane with $MesB(OMe)_2$ in Et_2O under reflux conditions (Scheme 1). Phosphaborin **1** was obtained as crystalline solids, which was stable against air and moisture in the solid state.[1]



SCHEME 1

The *P*-derivatives of **1** were synthesized using usual organophosphorus chemistry methods (Scheme 2).[2] The sulfide **2** and selenide **3** were obtained by the reaction of **1** with the corresponding elemental chalcogen in toluene. These reactions proceeded quantitatively, judging from the ^{31}P NMR spectra, but the moderate solubility of **2** and **3** may decrease the isolated yields. The reaction of **1** with BnBr gave the phosphonium salt **4**. These results indicate that the phosphorus atom of **1** has the same reactivity as that of ordinary triarylphosphines. The sulfide **2** and phosphonium salt **4** were pale yellow and colorless solids, respectively, but the selenide **3** was obtained as a yellow solid.



SCHEME 2

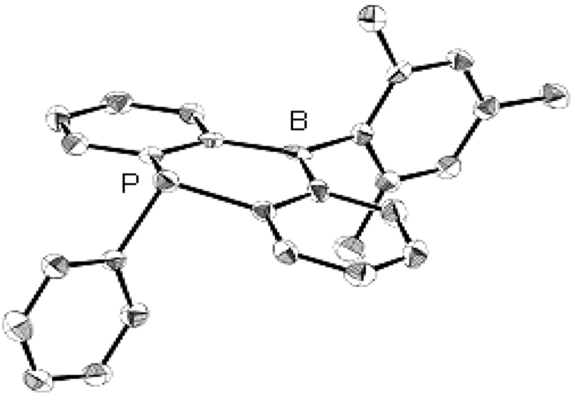


FIGURE 1 ORTEP drawing of dibenzophosphaborin 1.

Single crystals of **1** suitable for X-ray crystallographic analysis were obtained by recrystallization from benzene/Et_2O (Figure 1). Unlike the azaborine ring, the phosphaborin ring of **1** deviates from planarity due to pyramidalization at the phosphorus atom. The sums of the bond angles around the phosphorus atom (307°) and the boron atom (360°) are similar to those of ordinary triarylphosphanes and triarylboranes, respectively.

The UV-vis spectra of the dibenzopnictogenaborins and the dibenzophosphaborin *P*-derivatives were recorded in CH_2Cl_2 at 298 K (Table I). Dibenzoazaborine **5** showed an intense and sharp absorption profile in the violet to near UV region, but the UV-vis absorption of the phosphaborin **1** showed a weak and broad absorption, indicating a weaker donor-acceptor interaction between the phosphorus and boron atoms through π-conjugation, which was expected from the crystal structure described above. The phosphonium salt **4** showed an absorption maximum around 300 nm that is close to those of dibenzoborin **6** (λ_{max} 313 nm) and dibenzoxaborine **7** (λ_{max} 321 nm). Although the σ^*(P—Ph)

TABLE I UV-vis Spectral Data for Dibenzopnictogenaborins in CH_2Cl_2 at 298 K

Compound	λ/nm (ε/M^{-1} cm^{-1})
1	368 (5000)
5	404 (11600), 385 (9900)
2	353 (2000), 360 (1400)
3	369 (1300), 391 (1200)
4	312 (8000), 307 (7600), 381 (660)

TABLE II Complex Formation Constants $K(F^-)$ of Dibenzopnictogenaborins

Compound	$K(F^-)/M^{-1}$
1	$2.1(3) \times 10_4$
5	14(3)
2	$1.4(2) \times 10_5$
3	$3.3(7) \times 10_6$
4	–[a]

[a] The vale of $K(F^-)$ was too large to be determined.

orbital of **4** potentially works as an electron acceptor orbital, like the σ^*(Si-R) orbital of siloles or the σ^*(P-R) orbital of phospholes, these spectral data suggest that such electronic interactions are very weak in the case of **4**, and the phosphorus atom of **4** effectively functions as a bridging unit, like the carbon or oxygen atoms of **6** or **7**, respectively. Theoretical calculations on the phosphaborins also suggested that the P—Ph bonds of the phosphaborins do not function as acceptor orbitals. The dibenzophosphaborin chalcogenides **2** and **3** showed a weak absorption in near UV region, with intense absorption bands in the UV region. The absorption maximum of the selenide **3** was red-shifted compared to that of the sulfide **2**. These absorptions were assigned to the intramolecular charge transfer from the lone pair orbitals on the chalcogen atoms to the LUMOs that are constructed mainly from the boron 2p orbitals.

Dibenzoazaborine **5** exhibited moderately strong fluorescence in cyclohexane at 298 K (λ_{em} 421 nm,Φ 0.48), with a small Stokes shift ($\Delta\lambda$ 20 nm), indicating a retention of the rigid molecular structure in the excited state. However, the fluorescence of dibenzophosphaborin **1** and its *P*-derivatives was very weak ($\Phi < 0.01$), and the broadened spectral profiles, as well as the large Stokes shift ($\Delta\lambda > 100$ nm), revealed the existence of a substantial structural change after photoexcitation.

The complex formation constants between the dibenzoheteraborins and fluoride ion were determined from UV-vis titration experiments, and the results are summarized in Table II. The complex formation constants of dibenzoazaborine **5**, phosphaborin **1** and its sulfide **2** with fluoride ion increased in this order, reflecting the order of the calculated LUMO levels. The complex formation constant of the phosphonium salt **4** was too large to be determined under the same conditions.

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[1] T. Agou, J. Kobayashi, and T. Kawashima, *Org. Lett.*, **7,** 4373 (2005).
[2] T. Agou, J. Kobayashi, and T. Kawashima, *Inorg. Chem.*, **45,** 9137 (2006).