Heterocyclic Compounds

Synthesis of 1-Phospha-2-boraacenaphthenes: Reductive 1,2-Aryl Migration of 1-Diarylboryl-8-dichlorophosphinonaphthalenes**

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The chemistry of organic π -electron conjugated systems has attracted much attention in recent years from the viewpoint of material science, such as organic light-emitting diodes, photovoltaic cells, and liquid crystals. It is well known that the incorporation of main group elements into a π -electron conjugated backbone can effectively modify the electronic properties of a π -electron conjugated molecule.^[1,2] In particular, main group elements from groups 13 and 15 are employed in these systems because they can drastically change the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the π -conjugated systems as a result of the characteristic interactions of their vacant p orbital (group 13) and lone pair (group 15). With regard to this type of compound, azaborine,^[3] phosphaborine,^[4] boryl-substituted azobenzene,^[5] diborin,^[6] and ladder-type π -electron conjugated systems^[7] have been synthesized and revealed unique photophysical and electrochemical properties.

Phosphinoborane $(R_2P-BR'_2)^{[8]}$ is a heavier analogue of aminoborane $(R_2N-BR'_2)$, which exhibits an isoelectronic structure to an alkene $(R_2C=CR'_2)$. Theoretical calculations showed that the ground state of H_2P-BH_2 has a C_s symmetric structure with a pyramidal phosphorus atom; this structure is in contrast to the planar structure of the ground state of $H_2N BH_2$, which has $C_{2\nu}$ symmetry.^[9] Although H_2P-BH_2 and H_2N-BH_2 have different conformations in their ground states, their $H_2E=BH_2$ (E=N, P) π -bond energies are estimated to be almost the same (34 kcal mol⁻¹ for E=N, 36 kcal mol⁻¹ for E=P).^[9d,f] Thus, a P–B bond is a candidate to be a π -electron unit in π -electron conjugated systems. However, kinetic or thermodynamic stabilization would be necessary to isolate monomeric phosphinoborane as a stable

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compound, because phosphinoborane undergoes facile oligomerization in a head-to-tail manner by the formation of intermolecular P-B dative bonds.^[8a,10] A series of kinetically stabilized phosphinoboranes bearing mesityl, phenyl, trimethylsilyl, and 1-adamantyl groups have been reported by Power and co-workers,^[11] and phosphinoboranes ((LA)H₂P- $BH_2(LB)$; LA = Lewis acid, LB = Lewis base) that are thermodynamically stabilized by the coordination of a Lewis acid and base have been reported by Scheer and coworkers.^[12] We report herein the synthesis and properties of 1phospha-2-boraacenaphthene 1, which is a unique heterocyclic compound bearing a P-B bond attached to a naphthyl unit at the 1- and 8-positions.^[13] Compound 1 was synthesized by the reduction of 1-diarylboryl-8-dichlorophosphinonaphthalenes 2 by a unique intramolecular aryl migration from the boron atom to the phosphorus atom (Scheme 1).



Scheme 1. Synthesis of **1**. THF = tetrahydrofuran.

1-Diarylboryl-8-dichlorophosphinonaphthalenes **2** were synthesized from 1,8-dibromonaphthalene in two steps (Scheme 1). The reaction of 1,8-dibromonaphthalene with *n*BuLi and Ar₂BX (X = F or O*i*Pr; Ar = mesityl (**a**), 2,6dimethylphenyl (**b**), and 3,5-di-*tert*-butylphenyl (**c**)) in THF gave 1-bromo-8-diarylborylnaphthalenes **3** in moderate yields. Then, treatment of **3** with *n*BuLi at low temperature (-40 °C for **3a** and **3b**, and -78 °C for **3c**) followed by the addition of PCl₃ gave **2** in relatively high yields.^[14] It should be noted that the ¹¹B NMR spectra of **2a** and **2b** ($\delta = 63.9$ ppm for **2a**, $\delta = 64.3$ ppm for **2b**), and **2c** ($\delta = 10.1$ ppm) revealed the tri- (**2a** and **2b**) and tetra-coordination states (**2c**) of the boron atom. The steric repulsion resulting from the methyl groups on the aryl group of **2a** and **2b** is believed to prevent the formation of an intramolecular P–B dative bond.

The reduction of 2c with magnesium metal in THF at room temperature gave a mixture of two isomers, (E)-4c and (Z)-4c, which can be considered as dimers of the corresponding 1-phospha-2-boraacenaphthene 1c, in 35 and 53 % yields, respectively, upon isolation (Scheme 1).^[15,16] Therefore, the introduction of 3,5-*t*Bu₂C₆H₃ groups would not be suitable for the synthesis and isolation of a 1-phospha-2-boraacenaphthene in the monomeric form. On the other hand, the reduction of 2a and 2b with magnesium metal afforded 1a and 1b as orange crystals in 91 and 67 % yields, respectively, upon isolation.^[14] These results suggest it is necessary to have a substituent at the *ortho* positions of the aryl groups on the boron atom to isolate 1 as a stable compound. The monomeric molecular structure of 1a was unambiguously determined by X-ray crystallographic analysis (Figure 1).^[17] The deviation of



Figure 1. Molecular structure of **1 a** with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [deg], and dihedral angles [deg]: P(1)–B(1) 1.889(3), P(1)–C(1) 1.817(3), B(1)–C(9) 1.582(4); P(1)-C(1)-C(10) 108.59(17), B(1)-C(9)-C(10) 113.6(2), P(1)-C(1)···C(9)-B(1) 10.24(14).

the phosphorus atom from the naphthalene plane is 0.36 Å, while the boron atom is located on the same plane as naphthalene (Figure 1b). The sum of the bond angles around the phosphorus and boron atoms are 328.4(3)° and 359.5(6)°. respectively, thus confirming the pyramidal (phosphorus) and trigonal planar (boron) geometries. The P-B bond length in 1a is 1.889(3) Å, which is slightly longer than those in Mes_2PBMes_2 (6; 1.839(8) Å) and Ph_2PBMes_2 (7; 1.859(3) Å).^[11] The ¹¹B NMR spectra of 1a and 1b in C₆D₆ showed broad signals at $\delta_{\rm B} = 77.9$ ppm ($\Delta v_{1/2} = 1400$ Hz) for **1a** and $\delta_{\rm B} = 77.8$ ppm ($\Delta v_{1/2} = 930$ Hz) for **1b**, thus suggesting a trigonal planar geometry around the boron atom in solution. These values are similar to those of 6 ($\delta_{\rm B} = 82.4$ ppm) and 7 $(\delta_{\rm B} = 70.9 \text{ ppm}).^{[11]}$ On the other hand, the ³¹P NMR signals, observed at $\delta_{\rm P} = -28.2$ ppm (1a) and $\delta_{\rm P} = -27.7$ ppm (1b), were shifted relatively upfield compared to the signals of 6 $(\delta_P = 27.4 \text{ ppm})$ and 7 $(\delta_P = 26.7 \text{ ppm})$,^[11] probably due to the different geometries of the phosphorus atoms. That is, 1a exhibits the pyramidal geometry, and 6 exhibits almost planar geometry.^[8a] 1-Phospha-2-boraacenaphthenes 1a and 1b were stable under an inert atmosphere even on heating at 100 °C $(C_6D_6$ solution, sealed tube) for 24 h, but they underwent decomposition within three hours in dilute C₆D₆ solution at room temperature on exposure to air. The addition of degassed water into the C_6D_6 solution of **1a** afforded 1-hydroxy(mesityl)boryl-8-mesitylphosphinonaphthalene (**5a**) in 93 % yield.^[14]

A plausible mechanism for the formation of **1a**, **1b**, and **4c** is shown in Scheme 2. At first, the P–Cl bond of dichlorophosphine **2** could be reduced with magnesium



Scheme 2. Plausible mechanism for the formation of 1 and 4 from 2 by aryl migration from the boron atom to the phosphorus atom.

metal to give borate 8. Then, one of the two aryl groups on the boron atom in 8 migrates to the phosphorus atom to afford 1-phospha-2-boraacenaphthenes 1, together with the elimination of MgCl₂. Compounds 1a and 1b bearing mesityl or 2,6-dimethylphenyl were isolated as monomers, while 1c bearing 3,5-di-*tert*-butylphenyl groups is believed to undergo ready head-to-tail dimerization, thus leading to the formation of (E)-4c or (Z)-4c. When a 1:1 mixture of 2a and 2b was reduced under the same reaction conditions as used for the synthesis of 1, compounds 1a and 1b were obtained in a 1:1 ratio without the formation of any crossover product, as determined by the ¹H and ³¹P NMR spectra, thus suggesting the intramolecular migration of the aryl group in these reactions.^[14]

It is worth noting that compound **1a** was found to be orange in color, both in the crystalline form and in solution, in contrast to the previously reported phosphinoboranes, which were colorless or yellow crystals. Furthermore, **1a** exhibited weak but apparent orange emission in solution. Thus, we measured the cyclic voltammetry, UV/Vis, and emission spectra of **1a** to clarify the influence of the rigid geometry of the structure comprising of the P–B bond and the naphthyl moiety, to the electrochemical and photophysical properties of **1a**.^[18]

While **1a** showed an irreversible oxidation wave at $E_{\rm pa} = +$ 0.65 V (versus Fc/Fc⁺; Fc = ferrocene; Figure S1 in the Supporting Information), a reversible one-electron reduction couple was observed at $E_{\rm 1/2} = -2.22$ V together with an irreversible reduction wave at $E_{\rm pc} = -3.28$ V (versus Fc/Fc⁺; Figure S2 in the Supporting Information).^[14] The first reduction occurred at a less-negative region than that of dimesityl(1-naphthyl)borane (**9**; $E_{\rm 1/2} = -2.51$ V and $E_{\rm pc} = -3.30$ V) under the same reaction conditions.^[19] The less-negative reduction potential of **1a** compared to that of **9** is probably due to the very effective $p\pi - \pi^*$ conjugation between the naphthyl unit and the vacant p orbital of the boron atom; this conjugation could be a result of the rigid conformation, caused by the P–B bond attached to the naphthyl unit.

The UV/Vis spectra of 1a in hexane, THF, and CH_2Cl_2 solutions were similar to each other (Figure 2). In all cases,

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Figure 2. UV/Vis (black) and fluorescence (gray) spectra of 1 a in hexanes.

three characteristic absorption maxima were observed at 452 $(\varepsilon, 0.23-0.25 \times 10^4), 353 (\varepsilon, 0.61-0.63 \times 10^4), 302 (\varepsilon, 1.4-1.5 \times 10^4))$ 10⁴) together with 280 nm (sh, ε , 1.2–1.3×10⁴) as a shoulder.^[14,20] The longest absorption of **1a** is red-shifted in comparision with that of acenaphthene ($\lambda_{max} = 320 \text{ nm}$).^[21] Compound 1a showed a broad fluorescence spectrum in the range of ca. 510-750 nm.^[22] It should be noted that a subtle solvent effect [$\lambda_{max} = 595$ nm (hexane), 609 nm (THF), and 612 nm (CH₂Cl₂)] with the large Stokes shift ($\Delta = 5300$ -5700 cm⁻¹) suggested a large structural change between ground and excited states with the similar polarity. The observed lifetimes were 5.2, 1.5, and 3.6 ns, and the quantum yields were 0.032, 0.020, and 0.017 in hexane, THF, and CH_2Cl_2 , respectively. The calculated radiative (k_r) and nonradiative (k_{nr}) rate constants from the singlet excited state were $k_r = 6.1 \times 10^6$, $k_{nr} = 1.8 \times 10^8 \text{ s}^{-1}$ (hexane); $k_r = 1.3 \times 10^7$, $k_{\rm nr} = 6.5 \times 10^8 \, {\rm s}^{-1}$ (THF); and $k_{\rm r} = 4.7 \times 10^6$, $k_{\rm nr} = 2.7 \times 10^8 \, {\rm s}^{-1}$ (CH_2Cl_2) .^[23] The significantly small values of k_r compared to those of k_{nr} may retard the effective emission of **1a**.

Theoretical calculations of the ground (S₀) and excited (S_1) states of 1a (denoted as $1a(S_0)$ and $1a(S_1)$ hereafter) were performed at the B3LYP/def2-TZVPP level of theory with the TURBOMOLE program.^[24] The optimized structural parameters of $1a(S_0)$ are in good agreement with the experimentally observed parameters ($1a(S_0)$: P–B, 1.907 Å; P-C(Naph), 1.822 Å; B-C(Naph), 1.556 Å). The HOMO and LUMO of $1a(S_0)$ are shown in Figures 3 a and b, respectively. The HOMO of $1a(S_0)$, which is similar to that seen in H₂P-BH₂ with C_s symmetric structure,^[9a] exhibited a dominant contribution from the lone pair n orbital of the phosphorus atom (Figure 3a). On the other hand, the LUMO was the result of the vacant p orbital of the boron atom delocalized with the π^* orbital of the naphthalene unit, thus indicating an effective $p\pi-\pi^*$ conjugation (Figure 3b). TDDFT calculations for $\mathbf{1a}(S_0)$ ($\lambda = 475 \text{ nm}$ (f = 0.0185)) indicate that the longest absorption observed in the UV/Vis spectra ($\lambda =$ 452 nm) should be principally assignable to the intramolecular charge transfer from the phosphorus atom to the boron atom (HOMO-LUMO transition). It should be noted that the P-B, P-C(Naph), and B-C(Naph) bond lengths of $1a(S_1)$ were significantly different to those of $1a(S_0)$ (Figure 3c).^[14] The P–B bond length of $1a(S_1)$ (2.040 Å) is significantly longer than that of $1a(S_0)$ (1.907 Å), while the P–C(Naph) (1.780 Å) and B–C(Naph) (1.482 Å) bond lengths of $1a(S_1)$ are shorter than those of $1a(S_0)$ (P–C(Naph), 1.822 Å; B– C(Naph) 1.556 Å). Therefore, the phosphorus and boron atoms strongly interact with the naphthalene unit accompa-



Figure 3. a) HOMO of $1a(S_0)$ and b) LUMO of $1a(S_0)$ (isosurface at 0.04 a.u). c) Selected bond lengths of the optimized structures of $1a(S_0)$ (normal font) and $1a(S_1)$ (*italic font*). d) Schematic energy diagram for the ground (S_0) and excited (S_1) states of 1a. Mes=mesityl.

nied by a weakening of the P–B bond. Despite of the large structural changes, the HOMO and LUMO of $\mathbf{1a}(S_1)$ are similar to those of $\mathbf{1a}(S_0)$ (Figure S4 in the Supporting Information). TDDFT calculations for $\mathbf{1a}(S_1)$ predicted the wavelength and oscillation strength (*f*) of the HOMO– LUMO transitions in the excited state are 703 nm and 0.0146, respectively, thus supporting the large Stokes shift (calculated as $\Delta = 6800 \text{ cm}^{-1}$) and slow radiative process of **1** (Figure 3 d).^[25] While the theoretical results are somewhat red-shifted in comparison to the experimental transition energies, a result that is typical for DFT calculations in the case of charge-transfer (CT) excited states.

In summary, 1,2-diaryl-1-phospha-2-boraacenaphthenes **1a** and **1b** have been synthesized by the reduction of 1diarylboryl-8-dichlorophosphinonaphthalenes **2a** and **2b** by a unique intramolecular aryl migration from the boron atom to the phosphorus atom. Attractive electrochemical and photochemical properties of **1a** are provided by not only the intrinsic nature of the P–B bond but also the rigid conformation of the structure owing to the P–B bond being attached to the naphthyl unit at the 1- and 8-positions. This work provides insight into the intrinsic potential of a P–B bond in π -electron conjugated systems. Further investigations on the synthesis of such molecules are currently underway.

Experimental Section

Synthesis of **1a**: In a glovebox filled with argon, a solution of 1dichlorophophino-8-dimesitylborylnaphthalene (**2a**, 239 mg,



0.501 mmol) and magnesium metal (12.3 mg, 0.506 mmol) in THF (5 mL) was stirred at room temperature for 2 h. After the solvent was removed under reduced pressure, n-hexane was added to the residue, and then the mixture was filtered through Celite with hexanes. The filtrate was concentrated under reduced pressure, and the residue was washed with cooled hexanes to afford 1,2-dimesityl-1-phospha-2boraacenaphthene (1a, 185 mg, 0.455 mmol, 91%). 1a: orange crystals, m.p. 127 °C (decomp.). ¹H NMR (600 MHz, C_6D_6 , RT): $\delta =$ 2.02 (s, 3 H), 2.18 (s, 3 H), 2.280-2.282 (m, 6 H), 2.30 (s, 6 H), 6.67-6.68 (m, 2 H), 6.798–6.800 (m, 2 H), 7.28 (ddd, ${}^{3}J_{HH} = 8.2$ Hz, 7.0 Hz, ${}^{4}J_{HP} =$ 2.7 Hz, 1 H), 7.30 (dd, ${}^{3}J_{HH} = 8.2, 6.8$ Hz 1 H), 7.47 (ddd, ${}^{3}J_{HP} = 7.3$ Hz, ${}^{3}J_{\rm HH} = 7.0$ Hz, J = 1.0 Hz, 1 H), 7.55 (d, ${}^{3}J_{\rm HH} = 8.2$ Hz, 1 H), 7.75 (dd, ${}^{3}J_{\rm HH} = 8.2$ Hz, ${}^{4}J_{\rm HH} = 1.0$ Hz, 1 H), 7.89 ppm (ddd, ${}^{3}J_{\rm HH} = 6.8$ Hz, ${}^{4}J_{\rm HH} = 1.0$ Hz, ${}^{4}J_{\rm HP} = 1.0$ Hz, 1 H); ${}^{13}C{}^{1}H$ NMR (150 MHz, $C_{6}D_{6}$, RT): $\delta = 20.96$ (CH₃), 21.23 (CH₃), 23.72 (d, ${}^{4}J_{CP} = 4.6$ Hz, CH₃), 24.51 $(d, {}^{3}J_{CP} = 14.2 \text{ Hz}, \text{CH}_{3}), 126.26 \text{ (CH)}, 126.74, 127.17 \text{ (CH)}, 127.37 \text{ (d,}$ ${}^{3}J_{CP} = 7.7 \text{ Hz}, \text{ CH}$, 128.00 (CH), 128.76 (d, ${}^{2}J_{CP} = 10.9 \text{ Hz}, \text{ CH}$), 129.44 (d, ${}^{3}J_{CP} = 5.7$ Hz, CH), 132.09 (d, ${}^{3}J_{CP} = 1.9$ Hz), 133.81 (d, ${}^{4}J_{CP} = 1.8$ Hz, CH), 134.87 (d, ${}^{3}J_{CP} = 8.6$ Hz, CH), 137.52 (br), 137.57, 138.31 (d, ${}^{3}J_{CP} = 5.7 \text{ Hz}$), 139.01, 141.77 (d, ${}^{1}J_{CP} = 8.3 \text{ Hz}$), 142.66 (d, ${}^{2}J_{CP} = 17.6 \text{ Hz}$), 143.07 (br d, ${}^{2}J_{CP} = 12.0 \text{ Hz}$), 144.09 ppm (d, ${}^{2}J_{CP} =$ 12.9 Hz); ¹¹B NMR (95 MHz, C₆D₆, RT): $\delta = 77.6 (\Delta v_{1/2} = 1390 \text{ Hz});$ ³¹P NMR (121 MHz, C₆D₆, RT): $\delta = -28.2$ ppm. HRMS (FAB): *m*/*z*: calcd for $C_{28}H_{29}BP([M+H]^+)$: 407.2100; found: 407.2098 ($[M+H]^+$). Elemental analysis calcd (%) for C₂₈H₂₈BP: C 82.77, H 6.95%; found: C 82.80, H 6.96%. Assignment of the signals in ¹H and ¹³C NMR spectra is shown in the Supporting Information.

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