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Synthesis of 2-Alkenyl- and 2-Alkynyl-benzo[*b*]phospholes by Using Palladium-Catalyzed Cross-Coupling Reactions

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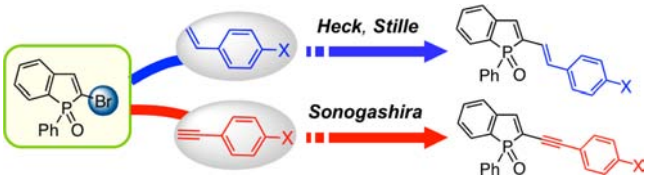
ABSTRACT



Heck, Stille, and Sonogashira reactions of 2-bromobenzo[*b*]phosphole *P*-oxide afforded a series of 2-alkenyl- and 2-alkynyl-benzo[*b*]phosphole *P*-oxides. The charge-transfer character of the new benzo[*b*]phosphole π-systems in the excited state is enhanced by the terminal electron-donating substituents. Furthermore, the C−Sn cross-coupling of the bromide was applied to the facile synthesis of a new Stille-coupling precursor, 2-stannylbenzo[*b*]phosphole.

Recently, much attention has been paid to phosphole-containing π-systems, which are promising candidates for a new class of phosphorus-based optical and electronic materials.[1] In particular, benzo[*b*]phospholes[2] and related compounds[3−7] have been continuously investigated because of their versatility in the introduction of various functional groups onto the α and β carbons of the phosphole unit to extend π-skeletons. Some π-extended and π-fused benzo[*b*]phosphole derivatives are known to

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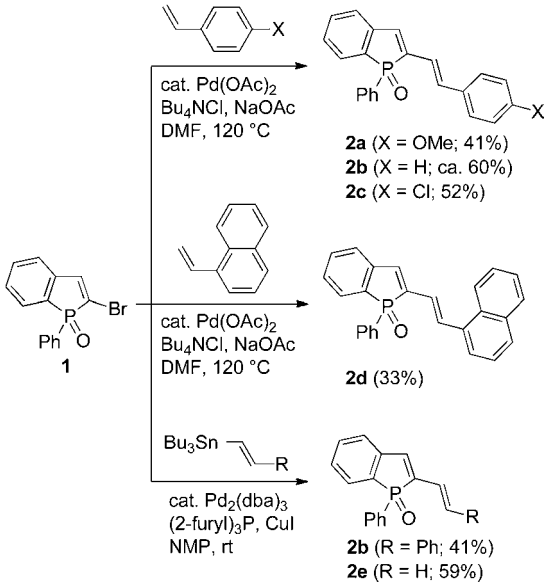
exhibit extremely high emitting abilities and/or high electron drift mobilities in the amorphous state.

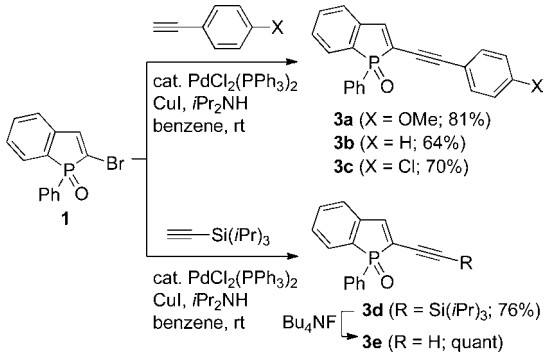
Most of the benzo[*b*]phosphole derivatives have been prepared by means of cycloaddition reactions of 2-alkynylphenyl(aryl)phosphines.[3,8,9] In this type of transformation, π-conjugative substituents should be incorporated into starting materials; it is necessary to prepare a 2-alkynylphenyl(aryl)phosphine for each benzo[*b*]phosphole. In 2012, we reported a new divergent method for the α-functionalization of a benzo[*b*]phosphole skeleton,[10] which was based on Stille coupling reactions of 2-bromobenzo[*b*]phosphole *P*-oxide[11] (**1**, in Scheme 1) with 2-stannylbenzo[*b*]heteroles. It was found that the benzo[*b*]phosphole−indole hybrid was highly fluorescent with large charge-transfer (CT) character in the excited state.[10] To our knowledge, however, the kind of π-conjugative substituents that have been introduced to the α position of the benzo[*b*]phosphole skeleton is still limited. Therefore, we have applied cross-coupling strategies to the syntheses of new kinds of π-extended benzo[*b*]phosphole derivatives. Herein, we report a series of 2-alkenyl- and 2-alkynyl-benzo[*b*]phospholes, which are available from **1** by using Stille, Heck, or Sonogashira reactions. The electronic effects of the vinylene/acetylene spacers and the *para*-substituents on the optical properties of the newly constructed π-systems are discussed comparatively. Furthermore, the C−Sn cross-coupling of **1** was applied to the facile synthesis of a new Stille-coupling precursor, 2-stannylbenzo[*b*]phosphole.

Scheme 1 summarizes the synthesis of 2-alkenylbenzo[*b*]phosphole *P*-oxides **2**. Treatment of the bromide **1** with four kinds of vinylarenes under a standard Heck condition [$Pd(OAc)_2$, Bu_4NCl, NaOAc, DMF at 120 °C] gave the corresponding 2-((*E*)-2-arylethenyl)benzo[*b*]phosphole *P*-oxides **2a**−**d** as the major products. The introduction of vinyl groups was also achieved by Stille coupling reactions of **1** with alkenyl(tributyl)stannanes, affording **2b** and **2e** in 41−59% yields. The bromide **1** also reacted with three kinds of arylacetylenes and triisopropylsilylacetylene under a standard Sonogashira condition [Pd, CuI, iPr_2NH, benzene at room temperature] to give the corresponding 2-alkynylbenzo[*b*]phosphole *P*-oxides **3a**−**d** in 64−81% yields (Scheme 2). The triisopropylsilyl group of **3d** was easily removed by treatment with Bu_4NF, generating the terminal free 2-ethynylbenzo[*b*]phosphole *P*-oxide **3e** in quantitative NMR yield.

Scheme 1. Synthesis of 2-Alkenylbenzo[*b*]phosphole *P*-Oxides



Scheme 2. Synthesis of 2-Alkynylbenzo[*b*]phosphole *P*-Oxides



The 2-substituted benzo[*b*]phosphole *P*-oxides **2** and **3** were characterized by using conventional spectroscopic techniques (NMR, HRMS, IR). The ^{31}P NMR peaks of **2** and **3** appeared at δ_P = 31.5−33.3 and 34.5−35.5 ppm, respectively. The structures of **2b**−**d** and **3b**,**c** were unambiguously elucidated by X-ray crystallography (Figures 1 and S1 in the Supporting Information).[12] The styryl derivatives **2b**,**c** possess highly planar frameworks with torsion angles at the inter-ring linkage (C1−C9−C10−C11) of ca. 179°, whereas the 2-(1-naphthyl)ethenyl derivative **2d** and the arylethynyl derivatives **3b**,**c** display twisted π-networks probably due to the crystal packing effects. In the crystalline states of **2b**−**d**, the vinylene-linked

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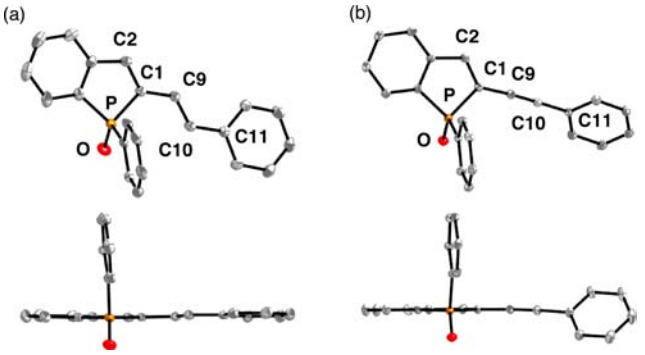


Figure 1. Crystal structures of (a) **2b** and (b) **3b**: Top views (upper) and side views (lower). Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): **2b**: P−O, 1.4859(10); C1−C2, 1.3510(19); C1−C9, 1.4414(19); C9−C10, 1.3421(19); C10−C11, 1.466(2); C1−C9−C10, 125.43(12); C9−C10−C11, 125.79(13); C2−C1−C9−C10, 177.03(13); C1−C9−C10−C11, 178.81(12). **3b**: P−O, 1.4827(8); C1−C2, 1.3499(16); C1−C9, 1.4196(16); C9−C10, 1.2013(17); C10−C11, 1.4375(17); C1−C9−C10, 175.93(12); C9−C10−C11, 178.07(13).

π-networks are partially stacked with the $\pi-\pi$ distances of 3.4−3.5 Å.

To understand the effects of the *para*-substituents and the π-spacers (vinylene, acetylene) on the optical and electrochemical properties of benzo[*b*]phosphole *P*-oxides, we measured absorption/emission spectra and redox potentials of **2** and **3** in CH_2Cl_2. The results are summarized in Figure 2 and Table 1. All the compounds examined are moderately to highly fluorescent in solution. In each series of the *para*-substituted derivatives (**2a**−**c** and **3a**−**c**), the absorption maxima (λ_{ab}) and emission maxima (λ_{em}) shift to longer wavelength with increasing the electron donating ability of the *para* substituents on the terminal benzene ring. In each series, the red shifts of the emission maxima are larger than those of the absorption maxima, suggesting that the excited singlet (S_1) states are more sensitive than the ground states to the *para*-substituent effects. In addition, the solvatochromism of the fluorescence spectra was

(12) **2b**: $C_{22}H_{17}OP$, MW = 328.33, 0.30 × 0.25 × 0.10 mm, monoclinic, $P2_1/c$, a = 9.308(2) Å, b = 11.131(2) Å, c = 17.312(4) Å, β = 103.927(3)°, V = 1741.0(6) Å^3, Z = 4, ρ_{calcd} = 1.253 g cm^{-3}, μ = 1.62 cm^{-1}, collected 13447, independent 3943, parameters 217, R_w = 0.0914, R = 0.0395 ($I > 2\sigma(I)$), GOF = 1.053. **2c**: $C_{22}H_{16}ClOP$, MW = 362.77, 0.40 × 0.15 × 0.10 mm, monoclinic, $P2_1/n$, a = 6.3504(2) Å, b = 7.9511(3) Å, c = 35.8818(12) Å, β = 94.457(2)°, V = 1806.29(11) Å^3, Z = 4, ρ_{calcd} = 1.334 g cm^{-3}, μ = 3.06 cm^{-1}, collected 14141, independent 4142, parameters 226, R_w = 0.0956, R = 0.0381 ($I > 2\sigma(I)$), GOF = 1.058. **2d**: $C_{26}H_{19}OP$, MW = 378.38, 0.35 × 0.20 × 0.15 mm, monoclinic, $P2_1/c$, a = 8.3951(13) Å, b = 8.9874(13) Å, c = 25.691(4) Å, β = 94.065(3)°, V = 1933.5(5) Å^3, Z = 4, ρ_{calcd} = 1.300 g cm^{-3}, μ = 1.56 cm^{-1}, collected 22777, independent 4418, parameters 253, R_w = 0.0917, R = 0.0368 ($I > 2\sigma(I)$), GOF = 1.090. **3b**: $C_{22}H_{15}OP$, MW = 326.31, 0.30 × 0.25 × 0.15 mm, monoclinic, $P2_1/c$, a = 7.9918(8) Å, b = 18.1517(17) Å, c = 11.7749(12) Å, β = 96.3610(10)°, V = 1697.6(3) Å^3, Z = 4, ρ_{calcd} = 1.277 g cm^{-3}, μ = 1.66 cm^{-1}, collected 13548, independent 3851, parameters 217, R_w = 0.0929, R = 0.0340 ($I > 2\sigma(I)$), GOF = 1.039. **3c**: $C_{22}H_{14}ClOP$, MW = 360.75, 0.30 × 0.20 × 0.10 mm, monoclinic, $P2_1/c$, a = 9.961(2) Å, b = 8.7326(17) Å, c = 21.055(4) Å, β = 102.507(3)°, V = 1788.0(6) Å^3, Z = 4, ρ_{calcd} = 1.340 g cm^{-3}, μ = 3.09 cm^{-1}, collected 13927, independent 4054, parameters 226, R_w = 0.0912, R = 0.0344 ($I > 2\sigma(I)$), GOF = 1.044.

Table 1. Optical Data and Redox Potentials of **2** and **3** in CH_2Cl_2

compd	λ_{ab}/nm (log ε)	λ_{em}/nm[a] (Φ_F)[b]	E_{ox}/V[c]	E_{red}/V[c]
2a	383 (4.31)	469 (0.73)	+0.77	−2.12
2b	367 (4.30)	446 (0.66)	+1.04	−2.07
2c	369 (4.40)	447 (0.60)	+1.12	−2.03
2d	376 (4.63)	468 (0.70)	+0.97	−2.05
2e	339 (3.79)	408 (0.81)	n.d.	−2.23
3a	374 (4.39)	455 (0.65)	+1.08	−2.02
3b	362 (4.25)	434 (0.77)	n.d.	−1.96
3c	361 (4.30)	437 (0.71)	n.d.	−1.95
3d	347 (3.97)	418 (0.69)	n.d.	−2.06

[a] Excited at λ_{ab}. [b] Absolute fluorescence quantum yields. [c] First oxidation (E_{ox}) and reduction (E_{red}) potentials (vs Fc/Fc^+) determined by DPV (0.1 M $Bu_4N^+PF_6^-$; Ag/Ag^+). n.d. = Not determined.

clearly observed for **2a**−**c** and **3a**−**c**, in which Stokes shifts increase with the increase of solvent polarity (Figures S2 and S3, Supporting Information). It should be noted that the changes in Stokes shifts of the *para*-methoxy derivatives (**2a** and **3a**) are larger than those of the *para*-chloro derivatives (**2c** and **3c**). Apparently, the CT character in the S_1 states of 2-alkenyl- and 2-alkynyl-benzo[*b*]phosphole *P*-oxides are appreciably enhanced when combined with the electron-donating *para*-methoxyphenyl groups; the benzo[*b*]phosphole unit behaves as the electron-accepting function. The λ_{ab} and λ_{em} values as well as the degree of solvatochromism ($\Delta\lambda_{em}$ = 1250 cm^{-1}) observed for **2a** are comparable to those for **3a** ($\Delta\lambda_{em}$ = 1250 cm^{-1}), suggesting that the linkage effects of the vinylene and acetylene spacers on the π-conjugation are close to each other. The electrochemical redox processes of **2** and **3** were measured by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). In the CV measurements, irreversible CV waves were observed for both oxidation and reduction processes (Figure S4, Supporting Information). As shown in Table 1, the *para*-substituents affect the oxidation potetials (E_{ox}) more efficiently than the reduction potentials (E_{red}). This is consistent with theoretical prediction (B3LYP/6-31G*); the orbital coefficient at the *para* carbon in HOMO is more distinct than that in LUMO (Figure S7, Supporting Information). The differences in the redox potentials ($E_{ox} - E_{red}$) increase in the order, **2a** (2.89 V) < **2b** (3.11 V) < **2c** (3.15 V) for the vinylene-linked series, which agrees well with the order of their HOMO−LUMO gaps obtained by the DFT calculations.

To attain some insight into excited-state dynamics of the newly constructed π-systems, we measured fluorescence lifetimes (τ_f) of **2a**−**e** and **3a**−**c** in CH_2Cl_2 at room temperature. The τ_f values of the styryl derivatives **2a**−**d** (2.7−3.7 ns) are comparable to those of the arylethynyl derivatives **3a**−**c** (3.0−3.9 ns). The radiative and nonradiative decay rate constants (k_r and k_{nr}) calculated from τ_f and Φ_f values are summarized in Table S2 in the Supporting Information. Among **2a**−**c** and **3a**−**c**, the effects of *para* substituents and π-spacers on the k_r values ($1.9-2.4 \times 10^8$ s^{-1}) are negligible compared to those on the k_{nr} values ($0.6-1.5 \times 10^8$ s^{-1}), although the absolute values

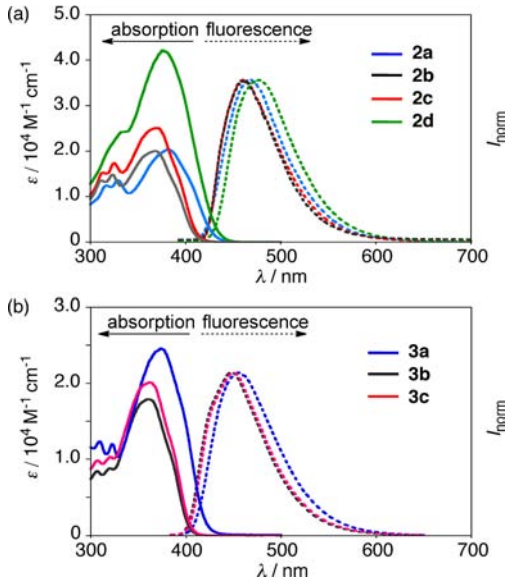


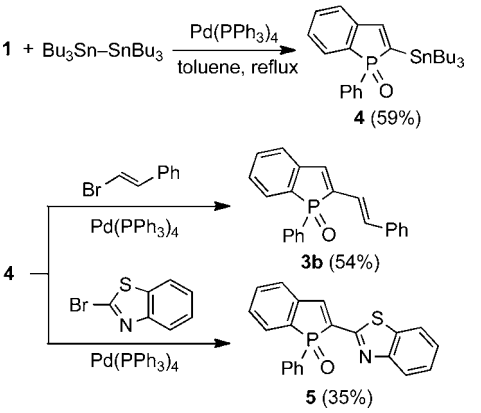
Figure 2. UV−vis absorption (dashed line) and emission spectra (dotted line, excited at the absorption maxima) of **2a**−**d** (a) and **3a**−**c** (b) in CH_2Cl_2.

of their differences are small. It is worth noting that the attachment of the phenyl group onto the vinyl function (**2a** vs **2e**) appreciably enhances the k_{nr} value (9.7×10^7 vs 2.0×10^7 s^{-1}). More efficient internal conversion and/or intersystem crossing with the increased vibrational mode as well as photochemical reactions may account for the acceleration of nonradiative decay from the S_1 state of **2a**−**d**.[13]

Furthermore, we conducted a Pd-catalyzed C−Sn cross-coupling reaction of **1** with hexabutyldistannane to obtain 2-stannylbenzo[*b*]phosphole *P*-oxide **4** as a new common precursor for Stille coupling reactions (Scheme 3). The desired stannylation occurred slowly under the Pd catalysis at reflux in toluene to give **4** in 59% yield. Subsequently, the 2-stannyl derivative **4** underwent Stille coupling with *β*-bromostyrene and 2-bromobenzothiazole to yield **3b** and benzo[*b*]phosphole−benzothiazole hybrid **5**,[10] respectively. These are the first examples of the C−C bond formation starting from 2-stannylbenzo[*b*]phosphole derivative.

(13) When irradiated in toluene with a high-pressure Hg arc lamp (>360 nm) for 1 h in an argon atmosphere, **2b** decomposed to some extent (judged by ^1H and ^{31}P NMR spectra).

Scheme 3. Synthesis of 2-(Tributylstannyl)benzo[*b*]phosphole **4** and Its Conversion to **3b** and **5**



In summary, we have established convenient and divergent methods for the synthesis of 2-alkenyl-, 2-alkynyl-, and 2-stannyl-benzo[*b*]phosphole *P*-oxides by using four kinds of cross-coupling reactions of 2-bromobenzo[*b*]phosphole *P*-oxide. The CT character of the vinylene- and acetylene-bridged benzo[*b*]phosphole *π*-systems in the excited state has proven to vary widely depending on the terminal *para*-substituents. With the present results in hand, a variety of *π*-conjugated benzo[*b*]phosphole derivatives are conceivable as functional dyes for use in organic electronic devices, and studies along this line are now in progress.

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Supporting Information Available. Experimental details, crystal structures, spectral data, CIF files, and DFT calculation results. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.