doi:10.1246/cl.2011.919
Published on the web September 5, 2011

Paper in Celebration for the 2010 Nobel Prize in Chemistry

Divergent Synthesis of 2,5-Diarylphospholes Based on Cross-coupling Reactions: Substituent Effects on the Optical and Redox Properties of Benzene–Phosphole–Benzene π-Systems

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Divergent synthesis of 2,5-diarylphosphole derivatives was achieved by using two kinds of Pd-catalyzed cross-coupling reactions. In addition, *para*- and *P*-substituent effects on the optical and redox properties of the benzene–phosphole–benzene π-systems were disclosed experimentally.

In recent years, π-conjugated phospholes have gained increasing attention as promising materials for applications in optoelectronics due to the characteristic properties of phosphole, such as high emitting ability, high electron-accepting ability, and versatile reactivity at phosphorus.[1] In particular, phospholes bearing aryl groups at the α (2,5-) positions have been frequently studied because polarizable and chemically tunable π-networks can be constructed by linking a phosphorus-bridged diene with arene functions. In this regard, several methods have been established for the synthesis of 2,5-diarylphospholes.[2] However, the number of aryl groups introduced to the α positions is still limited, and thereby the development of phosphole-based π-conjugated materials awaits a general method for the divergent synthesis of 2,5-diarylphospholes starting from readily accessible, common synthons.

Cross-coupling reactions,[3] which are among the most reliable methods to connect two different π-systems, have not been fully addressed in the synthesis of 2,5-diarylphospholes. This is partly due to the lack of information about the phosphole synthons that are applicable to cross-coupling conditions.[4–6] Recently, we succeeded in preparing the first example of α,α'-linked polyphosphole by using a Pd–CuI-promoted Stille-type coupling[7] between 2,5-bis(tributylstannyl)phosphole **1** and 2,5-diiodophosphole **2a** (Chart 1).[8,9] We envisioned that **1** as well as 2,5-dihalophospholes **2a** and **2b** would also be converted to a variety of 2,5-diarylphospholes by the cross-coupling methodology. Herein, we report the first divergent synthesis of 2,5-diarylphospholes bearing *para*-substituted phenyl, heteroaryl, or β-styryl groups starting from **1** or **2a**, **2b** based on the Stille and Negishi reactions. In addition, we have investigated *para*- and *P*-substituent effects on their optical and redox properties.

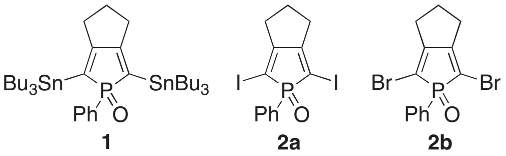
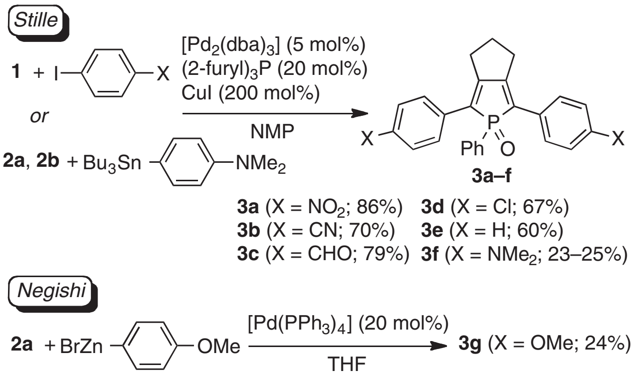
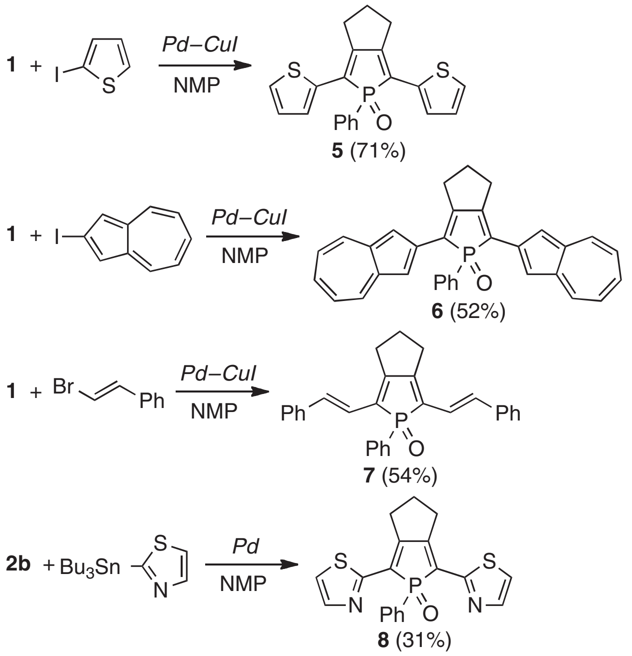


Chart 1.

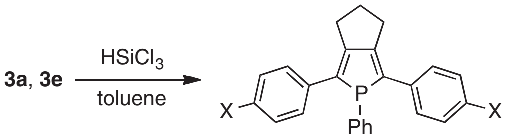


Scheme 1. Synthesis of 2,5-diarylphosphole *P*-oxides **3**.

Scheme 1 depicts the synthesis of 2,5-diarylphosphole *P*-oxides **3**. The starting materials **1** and **2a** were prepared according to a reported procedure.[8] The 2,5-dibromophosphole **2b** was newly prepared by bromolysis of **1** with NBS. Treatment of **1** with *p*-iodonitrobenzene in the presence of $[Pd_2(dba)_3]$ (5 mol %), tris(2-furyl)phosphine (20 mol %), and CuI (200 mol %) in *N*-methylpyrrolidone (NMP) at room temperature afforded 2,5-bis(*p*-nitrophenyl)phosphole *P*-oxide **3a** in 86% yield. Although we could not completely suppress the formation of a small amount of 2,2′-biphosphole (a homo-coupling product derived from **1**),[10] the target phosphole **3a** could be easily separated from this side product by column chromatography.[11] Therefore, we applied this Stille-type coupling to the synthesis of other 2,5-diarylphospholes. When **1** was treated with *p*-cyano-, *p*-formyl-, or *p*-chloroiodobenzene under the same Pd–CuI conditions, the corresponding 2,5-diarylphosphole *P*-oxides **3b**–**3d** were obtained in 67–79% yields. The conversion from **1**/iodobenzene to **3e**[12] was found to proceed smoothly at 80 °C. The Stille-type coupling also took place between **2a**, **2b** and tributyl(*p*-dimethylaminophenyl)stannane at 80 °C, affording **3f** in 23–25% yields. We further conducted Negishi coupling between **2a** and *p*-methoxyphenylzinc bromide in the presence of $[Pd(PPh_3)_4]$. In this reaction, the desired coupling product **3g** was isolated as the major product. Although the yield was not satisfactory in some cases, we have established a new, convenient method for the synthesis of a series of 2,5-diarylphosphole *P*-oxides. The successful isolation of **3a**–**3c** represents an advantage of the Pd-catalysis protocol, which allows delivery of reactive functions such as nitro, cyano, and formyl groups from the iodoarene substrates to the phosphole products.



Scheme 2. Synthesis of **5**–**8**. *Pd–CuI*: [$Pd_2(dba)_3$] (5 mol %), (2-furyl)$_3$P (20 mol %), CuI (200 mol %). *Pd*: [$Pd(PPh_3)_4$] (20 mol %).



(1)

4a (X = NO_2; 82%), **4e** (X = H; 71%)

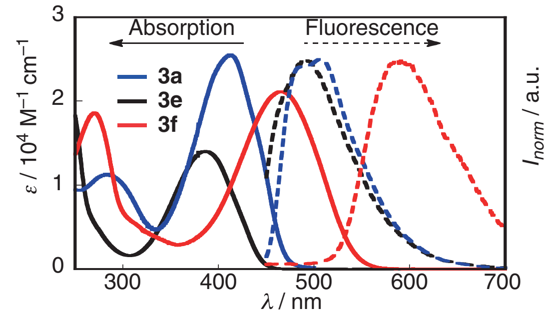


Figure 1. UV–vis absorption (solid line) and fluorescence (dashed line) spectra of **3a**, **3e**, and **3f** in CH_2Cl_2.

Table 1. Optical and electrochemical data for **3**–**8** in CH_2Cl_2

3–**8** (X)	λ_{ab}/nm (log ε)	λ_{em}/nm[a] (Φ_F[b])	τ_f/ns[a]	E_{red}/V[c]
3a (NO_2)	412 (4.41)	507 (0.30)	2.24	−1.37, −1.63
3b (CN)	394 (4.23)	496 (0.25)	2.29	−1.69, −1.93
3c (CHO)	407 (4.39)	504 (0.36)	2.09	−1.61, −1.73
3d (Cl)	392 (4.23)	500 (0.28)	1.97	−2.01
3e (H)[d]	387 (4.15)	491 (0.14)	1.39	−2.02
3f (NMe_2)	466 (4.33)	588 (0.01)	0.12	−2.05
3g (OMe)	411 (4.26)	525 (0.05)	0.52	−2.24
4a (NO_2)	423 (4.37)	527 (0.66)	2.50	−1.37, −2.15
4e (H)	369 (4.26)	452 (0.46)	2.41	−2.73
5	432 (4.24)	534 (0.04)	0.48	−2.09
6	481 (4.60)	N.f.[e] (—)	—	−1.56, −1.79
7	442 (4.43)	556 (0.17)	3.23	−1.84
8	424 (4.19)	519 (0.25)	1.95	−1.69, −2.08

[a] λ_{ex} = 400 (for **3a**–**3e**), 440 (for **3f**, **3g**, **4a**, **5**, **7**, and **8**), and 380 nm (for **4e**). [b] Absolute fluorescence quantum yields. [c] Determined by DPV (0.1 M n-Bu_4N^+ PF_6^-; Ag/Ag^+); Reduction potentials (E_{red}) vs. Fc/Fc^+. [d] Data from ref. 12. Φ_F was remeasured. [e] N.f.: Non-fluorescent.

When heated with excess trichlorosilane ($HSiCl_3$) in toluene at reflux, **3a** and **3e** were reduced at the phosphorus center to give σ^3-P derivatives **4a** and **4e**, respectively (eq 1). In addition to the *para*-substituted phenyl groups, 2-thienyl, 2-azulenyl, β-(E)-styryl, and 2-thiazolyl groups were introduced to the α-positions of the phosphole ring by the Stille-type coupling between **1** and the corresponding organyl halides or a Stille coupling between **2b** and 2-(tributylstannyl)thiazole, yielding 2,5-diorganylphospholes **5**–**8** in 31–71% yields (Scheme 2). Phosphole derivatives **3**–**8** were characterized by standard spectroscopic techniques. The ^{31}P NMR spectra of **3a**–**3g** showed singlet peaks at δ_P 53.6–55.1, indicating that the *para*-substituent effects on the ^{31}P chemical shifts are not significant. By contrast, the reductive deoxygenation from σ^4-P=O (**3a** and **3e**) to σ^3-P (**4a** and **4e**) induced upfield shift of the ^{31}P peak by ca. 20 ppm. The other phosphole *P*-oxides **5**–**8** displayed their ^{31}P resonances in the range of δ_P 50.8–53.8 ppm.

In order to reveal the optical properties of **3**–**8**, UV–vis absorption and fluorescence spectra were measured in CH_2Cl_2 (Figure 1, Figure S1 in the Supporting Information; SI,[16] and Table 1). The absorption and fluorescence maxima (λ_{ab} and λ_{em}) of the *para*-substituted diphenylphosphole derivatives **3a**–**3d**, **3f**, **3g** and **4a** are red-shifted relative to those of the unsubstituted references **3e** and **4e**. The λ_{ab} and λ_{em} values also depend on the α-substituents (**5**–**8** vs. **3e**). Among **3a**–**3g**, the red shifts of λ_{ab} and λ_{em} induced by the electron-donating substituents are larger than those induced by the electron-withdrawing groups, and the largest red shifts were observed for the σ^4-P=O/NMe_2 derivative **3f** ($\Delta\nu_{ab} = -4380\ cm^{-1}$ and $\Delta\nu_{em} = -3360\ cm^{-1}$ vs. **3e**). It is also noteworthy that the red shifts of the σ^3-P/NO_2 derivative **4a** ($\Delta\nu_{ab} = -3460\ cm^{-1}$ and $\Delta\nu_{em} = -3150\ cm^{-1}$ vs. **4e**) are much larger than those of the σ^4-P=O/NO_2 derivative **3a** ($\Delta\nu_{ab} = -1570\ cm^{-1}$ and $\Delta\nu_{em} = -640\ cm^{-1}$ vs. **3e**). This implies that the substituent effect of NO_2 groups on the HOMO–LUMO gap is enhanced by the *P*-deoxygenation. To get an additional insight into these spectral features, we carried out DFT calculations (B3LYP/6-31G*) of P–H models **3e-M**, **3f-M**, **4a-M**, and **4e-M** (Figure S2, Tables S1–S4 in SI[16]). In the optimized structure of **3f-M**, the HOMO is spread over the NMe_2 groups, whereas the LUMO is localized at the phosphole subunit. In **4a-M**, the LUMO is spread over the NO_2 groups, whereas the HOMO does not have electron density on them. The NMe_2-substitution destabilizes the HOMO more largely than the LUMO (**3f-M** vs. **3e-M**). By contrast, the NO_2-substitution stabilizes the LUMO more greatly than the HOMO (**4a-M** vs. **4e-M**). As a consequence, the HOMO–LUMO gaps become narrow for both *para*-substituted derivatives ($\Delta E_{H-L} = 3.08$ for **3f-M**; 2.97 eV for **4a-M**) relative to the unsubstituted references ($\Delta E_{H-L} = 3.32$ for **3e-M**; 3.71 eV for **4e-M**), which correlates well with the experimentally observed results. More importantly, the DFT calculations suggested that the HOMO–LUMO transitions in **3f** and **4a** possess intramolecular charge-transfer (CT) character.

To know the combined effects of the *para*- and *P*-substituents on the polarizability of 2,5-diarylphospholes, we measured solvatochromism of absorption and fluorescence spectra of **3e**, **3f**, **4a**, and **4e** using eight solvents with different polarity (Table S5 in SI[16]). With increasing the solvent polarity from cyclohexane ($\pi^* = 0$) to DMF ($\pi^* = 0.88$), $\lambda_{ab}/\lambda_{em}$ of **3f** and **4a** shifted to longer wavelength by 670/1810 and 1090/3230 cm^{-1}, respectively, showing a good linear correlation with π^*.[13] On the other hand, $\lambda_{ab}/\lambda_{em}$ of **3e** and **4e** were insensitive to the solvent polarity and almost constant. These results suggest that the combination of σ^4-P=O/NMe$_2$ (pull/push) or σ^3-P/NO$_2$ (push/pull) is effective for enhancing the polarizability of the benzene–phosphole–benzene π-systems. The larger solvent effect on λ_{em} than on λ_{ab} in the cases of **3f** and **4a** is indicative of the larger structural change in the excited state due to the CT character.

Except for **3f** and **6**, the present phosphole derivatives are moderately fluorescent with fluorescent quantum yields (Φ_f) of 0.04–0.66. To evaluate the substituent effects on the photophysical processes from excited singlet (S_1) states, fluorescence lifetimes (τ_f) were measured in CH_2Cl_2 at 22 °C. The fluorescence decays were well-fitted by the single-exponential component. As listed in Table 1, τ_f of **3a**–**3g** varied from 0.12 to 2.29 ns depending on the *para*-substituents. With Φ_f and τ_f values in hand, we calculated rate constants for radiative decay (k_r) and nonradiative decay (internal conversion and intersystem crossing, k_{nr}) from the S_1 states (Table S6 in SI[16]). In comparison with k_r and k_{nr} of **3e** (1.4×10^8 and $6.2 \times 10^8\ s^{-1}$, respectively), the *para*-substituent effects on k_r are small ($k_r = 0.8–1.7 \times 10^8\ s^{-1}$), while those on k_{nr} are relatively large ($k_{nr} = 3.1–83 \times 10^8\ s^{-1}$). It is likely that the substituent effects on Φ_f depend on the change in k_{nr} rather than the change in k_r. In particular, k_{nr} of **3f** and **3g** are 3–14 times as large as k_{nr} of **3e**, which suggests that the rotation at the NMe$_2$ and OMe groups in **3f** and **3g** accelerates the vibronic relaxation from their S_1 states in solution.[14]

The redox behavior of **3**–**8** was studied by cyclic voltammetry and differential pulse voltammetry (DPV). In most cases, electrochemical oxidations occurred irreversibly, whereas reductions occurred reversibly or quasi-reversibly. As summarized in Table 1, the introduction of the electron-withdrawing and electron-donating groups at *para*-positions causes anodic (for **3a**–**3d**) and cathodic (for **3f** and **3g**) shifts of the reduction potentials (E_{red}) over the range from $\Delta E_{red} = +0.39$ to -0.22 V (vs. **3e**).[15] As expected, the nitro groups made the most significant impact on the electron-accepting ability of the π-systems. The *P*-oxidation state (**4a** and **4e**) and the other α-substituents (**5**–**8**) also exhibited their own electronic effects on the redox properties.

In summary, we have established convenient methods for the divergent synthesis of 2,5-diarylphosphole derivatives based on cross-coupling reactions starting from the common phosphole synthons. The electronic effects of the *para*-substituents attached to the terminal α-phenyl groups on the optical and redox properties of the benzene–phosphole–benzene π-systems were evaluated for the first time. Notably, the chemical functionalization at the phosphorus center from σ^4-P=O to σ^3-P has proven to change the electron-donating/-accepting abilities as well as the polarizability of the whole π-systems. The present results provide valuable information about the synthesis and fundamental properties of phosphole-containing hybrid π-conjugates.

We thank Dr. Hirohiko Watanabe (Hamamatsu Photonics K.K.) for some photophysical measurements. This work was partially supported by Grants-in-Aid (Nos. 21108511 and 22350016) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan and Asahi glass foundation.

This paper is in celebration of the 2010 Nobel Prize awarded to Professors Richard F. Heck, Akira Suzuki, and Ei-ichi Negishi.

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14 Although we cannot exclude the contribution of intersystem crossing, no phosphorescence of **3g** was observed even at −196 °C.

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16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.