

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 coupling⁷ 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.

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 [Pd₂(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

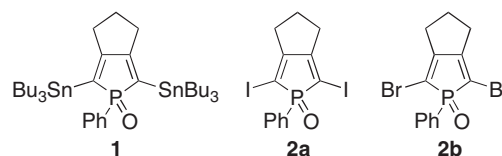
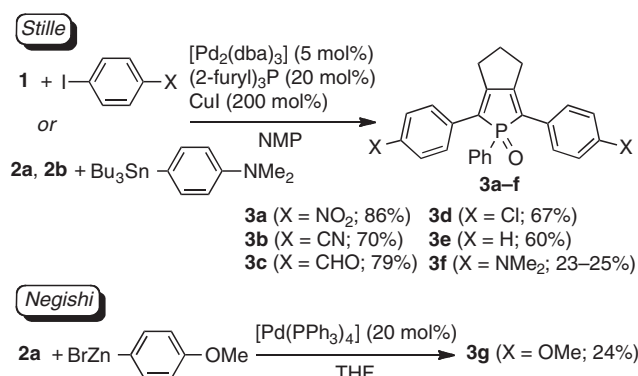
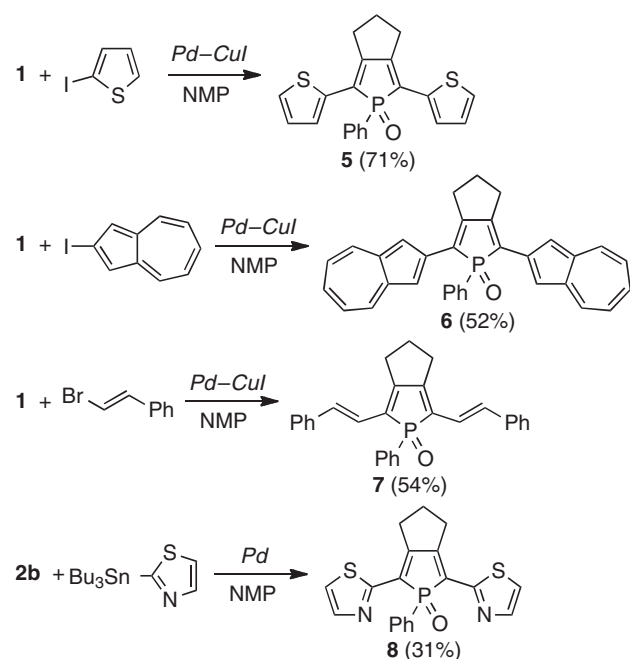


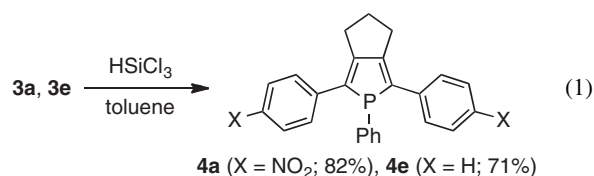
Chart 1.

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

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*-chloriodobenzene 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(PPh₃)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 : $[\text{Pd}_2(\text{dba})_3]$ (5 mol %), $(2\text{-furyl})_3\text{P}$ (20 mol %), CuI (200 mol %). Pd : $[\text{Pd}(\text{PPh}_3)_4]$ (20 mol %).



When heated with excess trichlorosilane (HSiCl_3) in toluene at reflux, **3a** and **3e** were reduced at the phosphorus center to give $\sigma^3\text{-P}$ 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 $\sigma^4\text{-P=O}$ (**3a** and **3e**) to $\sigma^3\text{-P}$ (**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 $\sigma^4\text{-P=O/NMe}_2$ derivative **3f** ($\Delta\nu_{\text{ab}} = -4380\text{ cm}^{-1}$ and $\Delta\nu_{\text{em}} = -3360\text{ cm}^{-1}$ vs. **3e**). It is also noteworthy that the red shifts of the $\sigma^3\text{-P/NO}_2$ derivative **4a**

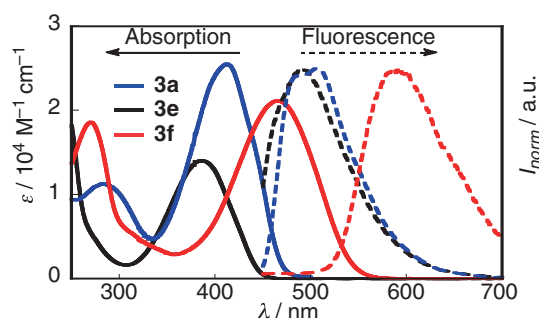


Figure 1. UV–vis absorption (solid line) and fluorescence (dashed line) spectra of **3a**, **3e**, and **3f** in CH_2Cl_2 .

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

3–8 (X)	$\lambda_{\text{ab}}/\text{nm}$ ($\log \epsilon$)	$\lambda_{\text{em}}/\text{nm}^a$ (Φ_{F}^b)	$\tau_{\text{f}}/\text{ns}^a$	$E_{\text{red}}/\text{V}^c$
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 $\lambda_{\text{ex}} = 400$ (for **3a–3e**), 440 (for **3f**, **3g**, **4a**, **5**, **7**, and **8**), and 380 nm (for **4e**). ^bAbsolute fluorescence quantum yields. ^cDetermined by DPV (0.1 M $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$; Ag/Ag^+); Reduction potentials (E_{red}) vs. Fc/Fc^+ . ^dData from ref. 12. Φ_{F} was remeasured. ^eN.f.: Non-fluorescent.

($\Delta\nu_{\text{ab}} = -3460\text{ cm}^{-1}$ and $\Delta\nu_{\text{em}} = -3150\text{ cm}^{-1}$ vs. **4e**) are much larger than those of the $\sigma^4\text{-P=O/NO}_2$ derivative **3a** ($\Delta\nu_{\text{ab}} = -1570\text{ cm}^{-1}$ and $\Delta\nu_{\text{em}} = -640\text{ cm}^{-1}$ 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 SI¹⁶). 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 ($\Delta E_{\text{H-L}} = 3.08$ for **3f-M**; 2.97 eV for **4a-M**) relative to the unsubstituted references ($\Delta E_{\text{H-L}} = 3.32$ 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 SI¹⁶). 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 $\sigma^4\text{-P=O/NMe}_2$ (pull/push) or $\sigma^3\text{-P/NO}_2$ (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 SI¹⁶). In comparison with k_r and k_{nr} of **3e** (1.4×10^8 and $6.2 \times 10^8 \text{ s}^{-1}$, respectively), the *para*-substituent effects on k_r are small ($k_r = 0.8\text{--}1.7 \times 10^8 \text{ s}^{-1}$), while those on k_{nr} are relatively large ($k_{nr} = 3.1\text{--}83 \times 10^8 \text{ s}^{-1}$). 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 $\sigma^4\text{-P=O}$ to $\sigma^3\text{-P}$ 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.

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- Although we cannot exclude the contribution of intersystem crossing, no phosphorescence of **3g** was observed even at -196°C .
- In **3a** and **4a**, electrochemical reductions of the nitro groups took place at $E_{red} = \text{ca. } -1.4 \text{ V}$.
- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.