JOC Note

A Convenient Method for the Synthesis of 2,5-Difunctionalized Phospholes Bearing Ester Groups

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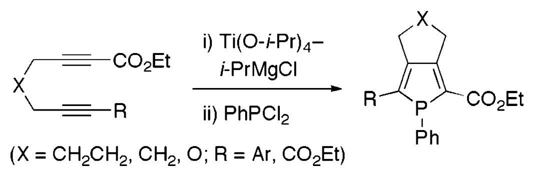
Received March 15, 2006



Symmetrically and unsymmetrically 2,5-difunctionalized phospholes bearing ester groups were prepared in a one-pot procedure from the corresponding diynes and dichloro(phenyl)phosphine via titanacyclopentadienes. The observed optical properties of the functionalized phospholes show that the π-conjugative push−pull interaction between the 2- and 5-substituents plays an important role in controlling the light-emitting efficiency.

The chemistry of phospholes has been the subject of numerous studies because of their utility as optical materials and P ligands.[1] It is well-known that the HOMO and LUMO energies and their energy gap, namely, optical and electrochemical properties, of phospholes are strongly dependent on the nature of the 2- and 5-substituents (α-substituents).[2] The coordinating ability of the phosphorus center of σ^3-phospholes is also influenced electronically and sterically by the α-substituents. In these respects, functionalization of the phosphole ring at the α-positions is a highly promising approach to design unexploited classes of phosphole-containing materials and catalysts. However, the number of phospholes bearing multiple carbonyl functionalities at the α-positions is still limited.[3] Burgada et al. and Tebby et al. independently reported the synthesis of phosphole-2,3,4,5-tetraesters by sequential addition−elimination reactions of trialkyl phosphites or dialkyl phosphonites with 2 equiv of dimethyl acetylenedicarboxylate.[4,5] Mathey and co-workers prepared a phosphole-2,5-dicarboxylic acid and its dimethyl ester via dilithiation of the corresponding 2,5-dibromophosphole.[6] Another interesting approach reported by Mathey's group involves potassium phospholides as key intermediates, from which several phosphole-2,5-dicarboxylic acids and esters are prepared via sequential [1,5]-sigmatropy of the functional groups.[7] Although these methods have their own synthetic merits, there is ample room for developing an efficient synthetic approach to this class of compounds. Here we report a new, convenient method for the synthesis of 1-phenylphosphole derivatives bearing one or two ester groups at the α-positions via titanacycles. The crystal structure, reactions, and optical properties of the newly prepared 2,5-difunctionalized phospholes are also described.

To obtain the target phosphole derivatives, we set out to use titanacyclopentadienes as key intermediates because this class of compounds is known as versatile precursors for various carbocyclic and heterocyclic compounds.[8,9] Quite recently, Tomita reported the synthesis of phosphole-containing polymers via titanacyclopentadienes, generated from phenylene-bridged diynes and Ti(II) reagents.[10] To our knowledge, however, Ti-

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[1] For reviews, see: (a) Quin, L. D. *The Heterocyclic Chemistry of Phosphorus*; Wiley: New York, 1981. (b) Mathey, F. *Chem. Rev.* **1988**, *88*, 429. (c) Mathey, F. *J. Organomet. Chem.* **1990**, *400*, 149. (d) Quin, L. D. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Elsevier: Oxford, 1996; Vol. 2. (e) Mathey, F.; Mercier, F. *C.R. Acad. Sci. Paris, Ser. IIb* **1997**, 701. (f) Hissler, M.; Dyer, P. W.; Réau, R. *Coord. Chem. Rev.* **2003**, *244*, 1. (g) Mathey, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578. (h) Mathey, F. *Acc. Chem. Res.* **2004**, *37*, 954. (i) Hissler, M.; Lescop, C.; Réau, R. *C.R. Chimie* **2005**, *8*, 1186.

[2] (a) Hay, C.; LeVilain, D.; Deborde, V.; Toupet, L.; Réau, R. *Chem. Commun.* **1999**, 345. (b) Hay, C.; Fischmeister, C.; Hissler, M.; Toupet, L.; Réau, R. *Angew. Chem., Int. Ed.* **2000**, *10*, 1812. (c) Hay, C.; Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nyulaszi, L.; Réau, R. *Chem.—Eur. J.* **2001**, *7*, 4222. (d) Delaere, D.; Nguyen, M. T.; Vanquickenborne, L. G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1522. (e) Delaere, D.; Nguyen, M. T.; Vanquickenborne, L. G. *J. Phys. Chem. A* **2003**, *107*, 838. (f) Su, H.-C.; Fadhel, O.; Yang, C.-J.; Cho, T.-Y.; Fave, C.; Hissler, M.; Wu, C.-C.; Réau, R. *J. Am. Chem. Soc.* **2006**, *128*, 983.

[3] Phospholes bearing one carbonyl functional group at the 2- or 5-position have been reported. (a) Mathey, F. *Tetrahedron Lett.* **1973**, 3255. (b) Mathey, F. *Tetrahedron* **1974**, *30*, 3127. (c) Mathey, F. *Tetrahedron* **1976**, *32*, 2395. (d) Santini, C. C.; Mathey, F. *J. Org. Chem.* **1985**, *50*, 467. (e) Deschamps, E.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992**, *129*, 486. (f) Deschamps, E.; Mathey, F. *Bull. Soc. Chim. Fr.* **1996**, *133*, 541. (g) Niemi, T.-A.; Coe, P. L.; Till, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1519. (h) Carmichael, D.; Klankermayer, J.; Richard, L.; Seeboth, N. *Chem. Commun.* **2004**, 1144.

[4] (a) Burgada, R.; Leroux, Y.; El Khoshnieh, Y. O. *Tetrahedron Lett.* **1981**, *22*, 3533. (b) Burgada, R.; El Khoshnieh, Y. O.; Leroux, Y. *Tetrahedron* **1985**, *41*, 1223.

[5] (a) Tebby, J. C.; Willetts, S. E.; Griffiths, D. V. *J. Chem. Soc., Chem. Commun.* **1981**, 420. (b) Caesar, J. C.; Griffiths, D. V.; Tebby, J. C.; Willetts, S. E. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1627. (c) Caesar, J. C.; Griffiths, D. V.; Tebby, J. C. *Phosphorus, Sulfur Silicon Relat. Elem.* **1987**, *29*, 123. (d) Caesar, J. C.; Griffiths, D. V.; Tebby, J. C. *J. Chem. Soc., Perkin Trans. 1* **1988**, 175.

[6] (a) Deschamps, É.; Mathey, F. *C.R. Acad. Sci. Paris Ser. IIc* **1998**, 715. (b) Deschamps, É.; Richard, L.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1158.

[7] (a) Holand, S.; Jeanjean, M.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 98. (b) Holand, S.; Maigrot, N.; Charrier, C.; Mathey, F. *Organometallics* **1998**, *17*, 2996. (c) Toullec, P.; Mathey, F. *Synlett* **2001**, 1977. (d) Melaimi, M.; Ricard, L.; Mathey, F.; Le Floch, P. *Org. Lett.* **2002**, *4*, 1245.

[8] For example, see: (a) Ohff, A.; Pulst, S.; Lefeber, C.; Peulecke, N.; Arndt, P.; Burkalov, V. V.; Rosenthal, U. *Synlett* **1996**, 111. (b) Whitby, R. J. *Transition Met. Org. Synth.* **1997**, 133. (c) Sato, F.; Urabe, H.; Okamoto, S. *Pure Appl. Chem.* **1999**, *71*, 1511. (d) Siebeneicher, H.; Doye, S. *J. Prakt. Chem.* **2000**, *342*, 102. (e) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835. (f) Mikami, K.; Matsumoto, Y.; Shiono, T. *Sci. Synth.* **2003**, *2*, 457. (g) Rosenthal, U.; Arndt, P.; Baumann, W.; Burlakov, V. V.; Spannenberg, A. *J. Organomet. Chem.* **2003**, *670*, 84.

[9] For the syntheses of 2,5-disubstituted phospholes via zirconacyclopentadienes (Fagan−Nugent method), see: (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Douglas, T.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1367. (c) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880. (d) Mao, S. S. H.; Tilley, T. D. *Macromolecules* **1997**, *30*, 5566. (e) Morisaki, Y.; Aiki, Y.; Chujo, Y. *Macromolecules* **2003**, *36*, 2594. See also ref 2.

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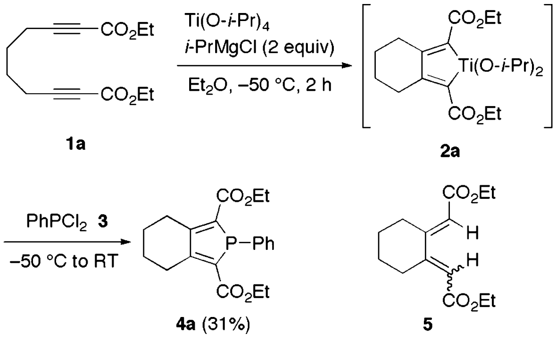
SCHEME 1. Synthesis of Phosphole 4a

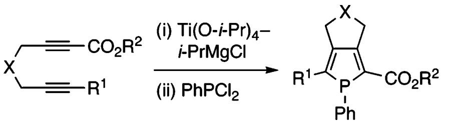


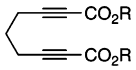
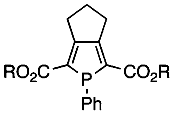
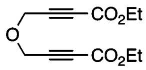
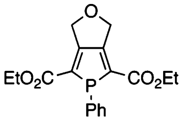
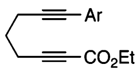
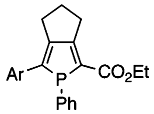
(II)-mediated cyclization of diynes bearing carbonyl groups at the terminal sp carbons to the corresponding 2,5-difunctionalized heteroles has not been examined so far. Scheme 1 depicts the synthesis of 1-phenylphosphole-2,5-dicarboxylic acid diethyl ester **4a**. Reaction of diethyl deca-2,8-diynedioate (**1a**) with (η^2-propene)Ti(O-*i*-Pr)$_2$, generated in situ from Ti(O-*i*-Pr)$_4$ and 2 equiv of *i*-PrMgCl as previously reported by Sato and coworkers,[11] followed by treatment with dichloro(phenyl)phosphine (**3**) afforded **4a** in 31% isolated yield. When the reaction was quenched by 1 M HCl without adding **3**, bis(ethoxycarbonylmethylene)cyclohexane (**5**)[12] was obtained as the hydrolyzed product. This result suggests that 2,5-bis(ethoxycarbonyl)-titanacyclopentadiene (**2a**) is formed by treatment of **1a** with (η^2-propene)Ti(O-*i*-Pr)$_2$ at −50 °C.[13] It should be noted here that the ester groups are compatible with the reaction conditions employed.[14]

Other symmetrically 2,5-difunctionalized phospholes **4b**−**d** were prepared from the corresponding diynedioates **1b**−**d** according to a similar procedure (Table 1, entries 2−4). Unsymmetrical diynes **1e**−**g** bearing an aryl group at one terminal and an ethoxycarbonyl group at the other were also converted to unsymmetrically 2,5-difunctionalized phospholes **4e**−**g** (entries 5−7). Attempts to convert 9-anthryl derivative **1h** to phosphole have been unsuccessful, probably due to steric reasons (entry 8). Although the isolated yields of **4a**−**g** are moderate, the present approach is convenient in that the desired phospholes are prepared from readily available substrates in a few steps.[15] Another practical advantage is that the symmetrical derivatives **4a**−**d** can be purified by simple recrystallization of the crude reaction mixture from MeOH without performing column chromatography. More importantly, it has been found that the Sato and Urabe titanacycle method is applicable to the synthesis of heteroles bearing one or two α-ester groups.

Compounds **4a**−**g** are air-stable solids and have been fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR, MS, IR, and elemental analyses. As was observed for the related bicyclic 1-phenyl-2,5-diarylphospholes,[2c] the ^{31}P and ^{13}C chemical shifts of the phosphole ring are strongly influenced by the fused carbocycle. Thus, the ^{31}P NMR peaks of the 3,4-C$_3$-bridged derivatives **4b**−**g** were observed at much lower fields ($\delta = +32.0-40.5$) than that of the 3,4-C$_4$-bridged derivative **4a** ($\delta = +8.7$). The β-carbons (C3 and C4 carbons) are much more deshielded than the α-carbons (C2 and C5 carbons) for **4b**−**g**, whereas there is a slight difference in their chemical shifts for **4a**. These data imply that the fused carbocycle constrains the structural modification of the phosphole ring to some extent. On the other hand, the carbonyl carbons of **4a**−**g** were observed at almost the same field ($\delta = 163.8-165.1$) with relatively large $^2J_{\mathrm{P-C}}$ values of 15.6−21.7 Hz.

TABLE 1. Synthesis of 2,5-Difunctionalized Phospholes 4



entry	diyne **1**	phosphole **4** (yield/%)
1	**1a**	**4a** (31%)
		
2	**1b** (R = Et)	**4b** (50%)
3	**1c** (R = Me)	**4c** (42%)
4	 **1d**	 **4d** (23%)
		
5	**1e** (Ar = Ph)	**4e** (27%)
6	**1f** (Ar = 2-pyridyl)	**4f** (40%)
7	**1g** (Ar = 2-thienyl)	**4g** (44%)
8	**1h** (Ar = 9-anthryl)	not obtained

The structure of diester **4b** was further elucidated by X-ray crystallographic analysis (Figure 1).[16] The phosphorus center adopts a distorted trigonal pyramidal geometry with a mean C−P−C angle of 98.1°. The average C$_\alpha$−C$_\beta$ bond length of 1.36 Å is much shorter than the C$_\beta$−C$_\beta$ bond length of 1.456(2) Å, and the Bird index was calculated to be 25.6,[17] indicating the low aromaticity of the phosphole ring in **4b**. Two carbonyl groups lie on almost the same plane of the phosphole ring, probably due to the π-conjugation with the adjacent C$_\alpha$−C$_\beta$ double bonds.

Compounds **4** are potential precursors for other 2,5-difunctionalized phospholes. Some chemical transformations at the ester groups and/or the phosphorus center of **4b** and **4g** are summarized in Scheme 2. Reaction of **4b** with an excess amount

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[10] (a) Tomita, I.; Ueda, M. *Macromol. Symp.* **2004**, *209*, 217. (b) Tomita, I. *Polym. Prep.* **2004**, *45*, 415.

[11] (a) Urabe, H.; Suzuki, K.; Sato, F. *J. Am. Chem. Soc.* **1997**, *119*, 10014. (b) Urabe, H.; Takeda, T.; Hideura, D.; Sato, F. *J. Am. Chem. Soc.* **1997**, *119*, 11295.

[12] Kawasaki, T.; Saito, S.; Yamamoto, Y. *J. Org. Chem.* **2002**, *67*, 4911.

[13] In this reaction, the temperature should be kept at −50 °C during the formation of the titanacycle. Below or above this temperature, the yield of **4a** decreased significantly.

[14] (a) Boymond, L.; Rottländer, M.; Cahiez, G.; Knochel P. *Angew. Chem., Int. Ed.* **1998**, *37*, 1701. (b) Ren, H.; Krasovskiy, A.; Knochel, P. *Org. Lett.* **2004**, *6*, 4215. (c) Knochel, P.; Dohle, W.; Gommermann, N.; Kneisel, F. F.; Kopp, F.; Korn, T.; Sapountzis, I.; Vu, V. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 4302.

[15] Compounds **1a**−**h** were prepared from the corresponding terminal-free diynes in one or two steps.

[16] Formula $C_{19}H_{21}O_4P$, space group $P2_1/a$, $a = 9.350(3)$ Å, $b = 20.265(6)$ Å, $c = 9.951(3)$ Å, $\beta = 113.1422(11)°$, $V = 1733.7(10)$ Å^3, $Z = 4$, $D_c = 1.319$ g cm^{-3}, 13 544 observed and 218 variables, $R_w = 0.1221$, $R = 0.0503$ ($I > 2.00\sigma(I)$), GOF = 1.16.

[17] (a) Bird, C. W. *Tetrahedron* **1985**, *41*, 1409. (b) Bird, C. W. *Tetrahedron* **1990**, *46*, 5697.

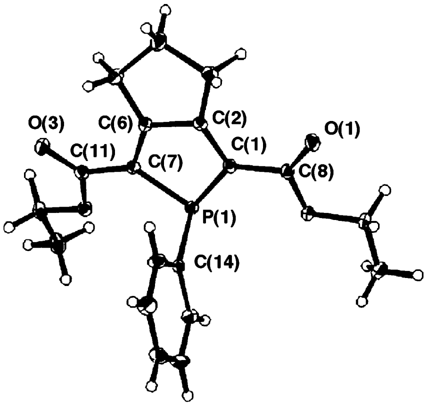
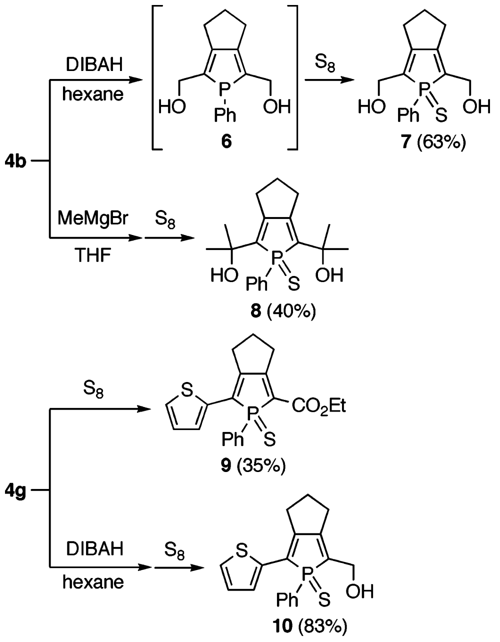


FIGURE 1. ORTEP diagram of **4b** (30% probability ellipsoids). Selected bond lengths (Å) and bond angles (deg): P1−C1, 1.820(2); P1−C7, 1.8200(19); P1−C14, 1.8417(17); C1−C2, 1.357(2); C2−C6, 1.456(2); C6−C7, 1.359(3); C1−C8, 1.475(2); C7−C11, 1.478(2); O1−C8, 1.211(2); O2−C9, 1.459(2); C1−P1−C7, 89.88(9); C1−P1−C14, 102.12(8); C7−P1−C14, 102.16(8).

SCHEME 2. Functionalization of Phospholes 4b,g



of diisobutylaluminum hydride (DIBAH) in hexane gave 2,5-bis(hydroxymethyl)phosphole **6** as a moderately air-sensitive substance.[18] The subsequent treatment of **6** with elemental sulfur (S_8) afforded the corresponding phosphine sulfide **7** as an air-stable solid in 63% total yield (from **4b**). Treatment of **4b** with 4 equiv of MeMgBr in THF, followed by addition of S_8, gave tertiary diol **8** in 40% yield. The diols **7** and **8** are potential precursors for phosphole-containing macrocyclic compounds. When treated with excess S_8 in CH_2Cl_2 at room temperature for 5 days, **4g** was converted to the phosphine sulfide **9** in 35% yield. Under the same conditions, diester **4b** was recovered quantitatively. The thienyl ester **4g** also reacted with DIBAH/S_8 to give primary alcohol **10** in 83% yield. The ^{31}P chemical shifts of the σ^4-phospholes **7**−**10** were observed at fields lower ($\delta = +66.2-68.9$) than those of the σ^3-phospholes **4b** and **4g**.

To examine the substituent effects on the optical properties of the 2,5-difunctionalized phospholes, UV−vis absorption and fluorescence spectra of **4b**, **4e**−**g**, **9**, and **10** were measured in THF (Table 2). The absorption maximum due to the $\pi-\pi^*$ transition of the extended conjugated system of thienyl ester **4g** ($\lambda_{max} = 382$ nm) is red shifted relative to those of phenyl and pyridyl esters **4e**,**f** ($\lambda_{max} = 355$ and 357 nm, respectively) and diester **4b** ($\lambda_{max} = 329$ nm). The functionalization at phosphorus from σ^3 to σ^4 (**9** vs **4g**) causes a slight red shift, whereas the replacement of the ester group by the hydroxymethyl group (**10** vs **9**) causes a blue shift. Significant substituent effects were also observed in the fluorescence spectra. The σ^3-types of phenyl and thienyl esters **4e** and **4g** are moderately fluorescent,[19] wherein **4g** exhibits an emission band at a longer wavelength ($\lambda_{max} = 475$ nm) than **4e** ($\lambda_{max} = 453$ nm). In contrast, the other phospholes examined are weakly fluorescent (**4f**) or nonfluorescent (**4b**, **9**, **10**). These data clearly show that the electronic properties of the α-substituents and the phosphorus center affect the degree of π-conjugation with the 1,3-diene unit of the phosphole ring. More importantly, the π-conjugative push−pull (charge-transfer) interaction between the electron-donating 5-aryl group and the electron-withdrawing 2-ester group plays an important role in controlling the HOMO−LUMO gap of 2,5-difunctionalized phospholes and their light-emitting efficiencies.[20] To compare the polarity in the excited state with that in the ground state, the solvatochromism of the absorption and fluorescence spectra of **4g** was also examined. Thus, when the solvent was changed from cyclohexane to *N*,*N*-dimethylformamide (DMF), the emission maxima of **4g** displayed a larger bathochromic shift ($\Delta\lambda_{em} = 1263$ cm^{-1}) than the absorption maxima ($\Delta\lambda_{max} = 478$ cm^{-1}).[21] A Kamlet−Taft analysis[22] for the fluorescence spectra gave a linear solvation energy relationship (LSER) versus the solvatochromic parameter π^* [$\nu_{em} = 21.80-1.29\pi^*$ (10^3 cm^{-1})] with an *R* value of 0.973 ($n = 11$). Although a reliable LSER could not be given from the absorption spectra, it is apparent that the polarity of the excited state of **4g** is larger than that of the ground state.

TABLE 2. Absorption and Fluorescence Spectra of 2,5-Difunctionalized Phospholes[a]

phosphole	λ_{max}/nm (log ϵ)	λ_{em}/nm[b]
4b	329 (3.92)	*c*
4e	355 (4.12)	453
4f	357 (4.18)	*d*
4g	382 (4.17)	475
9	390 (4.03)	*c*
10	375 (3.87)	*c*

[a] Measured in THF at 25 °C. [b] Excited at 365 nm. [c] No emission was detected. [d] A weak and broad band was observed at around 585 nm.

In summary, we have demonstrated for the first time that the diynes bearing one or two terminal ester groups are successfully transformed to the corresponding 2,5-difunctionalized phospholes via titanacyclopentadiene intermediates. A practical

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(18) Compound **6** was characterized by ^{1}H NMR and mass spectrometry.

(19) Fluorescence quantum yields of **4e** and **4g** relative to quinine sulfate were determined to be 0.074 and 0.088%, respectively.

(20) Reáu and co-workers have extensively studied the optical properties of 2,5-diarylphosphole derivatives and disclosed the important role of an intramolecular charge-transfer interaction enforced by the presence of different types of aryl substituents, such as thienyl and pyridyl groups. See: (a) Fave, C.; Hissler, M.; Sénéchal, K.; Ledoux, I.; Zyss, J.; Réau, R. *Chem. Commun.* **2002**, 1674. (b) Hay, C.; Sauthier, M.; Deborde, V.; Hissler, M.; Toupet, L.; Reáu, R. *J. Organomet. Chem.* **2002**, *643−644*, 494.

(21) Solvatochromism of the absorption and emission bands (λ_{max}, λ_{em}) of **4g** (nm): cyclohexane (379, 457); Et_3N (380, 465); Et_2O (379, 468); CCl_4 (383, 464); EtOAc (386, 473); THF (382, 475); $CHCl_3$ (385, 477); acetone (381, 478); MeCN (380, 482); CH_2Cl_2 (382, 479); DMF (384, 485).

(22) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

advantage of the present method is that the starting substrates are readily accessible from commercially available materials. Furthermore, the present method is potentially applicable to the synthesis of other heterocyclic compounds bearing α-ester groups. The observed optical properties of newly prepared 2,5-difunctionalized phospholes demonstrate that a combination of the 2-ester group and the electron-donating 5-aryl group contributes to the efficient π-conjugative interaction with the phosphole ring.

Experimental Section

To a mixture of **1a** (1.25 g, 5.0 mmol), Ti(O-*i*-Pr)$_4$ (1.5 mL, 5.0 mmol), and Et$_2$O (75 mL) was slowly added an ether solution of *i*-PrMgCl (2.0 M × 5.0 mL, 10 mmol) at −78 °C, and the resulting mixture was stirred for 2 h at −50 °C. Dichloro(phenyl)phosphine **3** (0.68 mL, 5.0 mmol) was then added to the mixture at this temperature, and the resulting suspension was allowed to warm to room temperature. After stirring for an additional 2 h at room temperature, a saturated NH$_4$Cl solution (30 mL) was poured into the reaction mixture, and insoluble substances were filtered off through a Celite bed. The filtrate was separated, and the aqueous phase was extracted with Et$_2$O (15 mL × 2). The combined organic extracts were washed with brine (50 mL), dried over MgSO$_4$, and concentrated in vacuo to give an oily residue, which was crystallized from cold MeOH at −78 °C to afford **4a** (560 mg, 31%) as a pale yellow solid. When the reaction was quenched without adding **3**, cyclic olefin **5** was obtained as the major product.

4a: Mp 71−72 °C; ^{1}H NMR (CDCl$_3$) δ 1.10 (t, 6H, $J = 6.8$ Hz), 1.76 (br, 4H), 3.03 (br, 2H), 3.21 (br, 2H), 4.11 (br, 4H), 7.25−7.35 (m, 5H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 14.1, 22.2, 29.0, 60.3, 128.3 (d, $^3J_{P-C} = 8.7$ Hz), 129.8 (d, $^4J_{P-C} = 1.9$ Hz), 134.0 (d, $^2J_{P-C} = 19.9$ Hz), 136.9, 158.8 (d, $^2J_{P-C} = 10.6$ Hz), 164.8 (d, $^2J_{P-C} = 18.8$ Hz); ^{31}P{^{1}H} NMR (CDCl$_3$) $\delta + 8.7$; IR (KBr) ν_{max} 1701, 1696 (C═O) cm^{-1}; MS (MALDI-TOF) *m/z* 358 (M$^+$). Anal. Calcd for $C_{12}H_{23}O_4P$: C, 67.03; H, 6.47; P, 8.64. Found: C, 67.21; H, 6.51; P, 8.44. The *ipso* carbon of the phenyl group could not be detected clearly in the ^{13}C NMR.

5. (1*E*,2*E*)-Isomer: ^{1}H NMR (CDCl$_3$) δ 1.29 (t, 6H, $J = 6.8$ Hz), 1.74 (m, 4H), 2.98 (m, 4H), 4.15 (q, 4H, $J = 6.8$ Hz), 5.83 (s, 2H). (1*E*,2*Z*)-Isomer: ^{1}H NMR (CDCl$_3$) δ 1.23 (t, 6H, $J = 6.8$ Hz), 1.74 (m, 4H), 2.37 (m, 4H), 4.21 (q, 4H, $J = 6.8$ Hz), 5.61 (s, 1H), 5.66 (s, 1H).

Acknowledgment. This work was partially supported by a Grant-in-Aid (No. 17350018) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Supporting Information Available: Experimental details, full spectroscopic data, and the CIF file of **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0605748