JOC Article

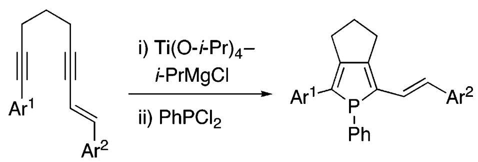
Synthesis of 2-Aryl-5-styrylphospholes: Promising Candidates for the Phosphole-Based NLO Chromophores

Yoshihiro Matano,*,† Tooru Miyajima,† Hiroshi Imahori,† and Yoshifumi Kimura‡

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan, and Division of Research Initiatives, International Innovation Center, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

matano@scl.kyoto-u.ac.jp

Received April 19, 2007



2-Aryl-1-phenyl-5-styrylphospholes were prepared in good yields in a one-pot procedure from the corresponding 1,9-diarylnona-8-ene-1,6-diynes and dichloro(phenyl)phosphine via intermediary titanacyclopentadienes. According to the UV−vis absorption and fluorescence spectra of this class of compounds, the optical properties of the phosphole−vinylene-bridged π-conjugated system have been revealed to depend strongly on the electronic character of the terminal functionalities. In particular, the polarizability at the excited-state has been found to be considerably greater than that in the ground state. High molecular hyperpolarizabilities obtained for the push−pull type of 2-aryl-5-styrylphospholes in the hyper-Rayleigh scattering measurements demonstrate the potential utility of the stilbene-type phosphole derivatives as a new class of second-order NLO chromophores.

Introduction

Phosphole is known as a basically nonaromatic heterole and to possess the polarizable and electron excessive *cis*-dienic π-system connected by a phosphorus atom. As a consequence, phospholes exhibit characteristic optical and electrochemical properties that differ considerably from those of pyrroles.[1] Both experimental and theoretical studies have revealed that π-conjugated substituents attached at the 2- and 5-positions (α positions) of the phosphole ring play an important role in controlling the HOMO and LUMO energies as well as the polarizability of the *cis*-dienic π-system of phospholes.[2] In particular, unsymmetrically substituted phospholes bearing electron donor (D) and electron acceptor (A) functionalities at the α positions have been suggested to act as nonlinear optics (NLO). In 1997, Marks and co-workers reported quantitative analysis of aromaticity and auxiliary D−A effects on molecular hyperpolarizabilities of several π-conjugated stilbene-type chromophores, including phosphole derivatives, based on theoretical calculations. They concluded that electron density of the heterocycles plays the major role in determining second-order NLO response properties.[3] For instance, model compound **1a** (Figure 1), in which the phosphole ring acts as an electron-excessive heterocycle, was predicted to exhibit higher NLO responses than the thiophene analogue.[4] The high electron-excessive nature of the phosphole ring was further confirmed by comparing the hyperpolarizability of the D−phosphole−

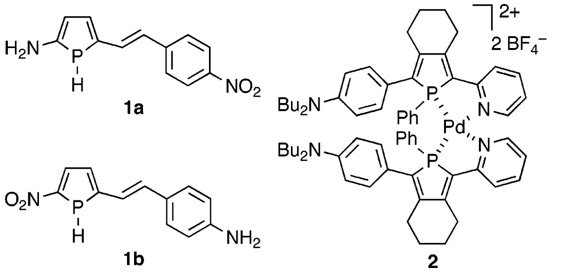


FIGURE 1. Phosphole-based NLO chromophores.

---

* Corresponding author. Phone: 81 75 383 2567. Fax: 81 75 383 2571.

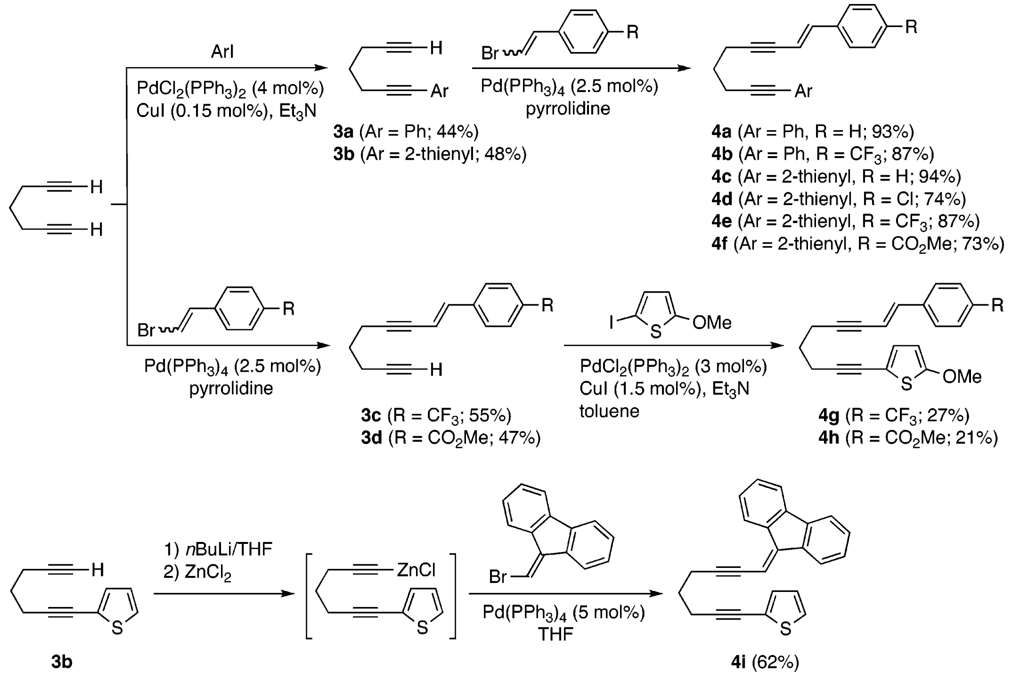
† Graduate School of Engineering.

‡ International Innovation Center.

(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, Sér. II b* **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.

10.1021/jo070822f CCC: $37.00

SCHEME 1. Synthesis of 4a−i



vinylene−benzene−A system **1a** with that of the reverse dipolar system **1b**. Thus, to enhance the second-order NLO response properties of the stilbene-type phosphole derivatives, it would be desirable to attach an electron-donating group at the phosphole terminus and an electron-withdrawing group at the benzene terminus. In 2002, Réau and co-workers experimentally determined molecular hyperpolarizabilities of phosphole derivatives for the first time. Interestingly, the NLO responses of 5-aryl-2-(2-pyridyl)phospholes are enhanced remarkably by the stereoselective complexation with a cationic palladium(II) salt through P,N-chelates.[5] For example, the cationic complex **2** exhibits a β value of 180 $\times$ 10^{-30} esu (at 1.91 μm), which is much larger than the sum over the contribution of two subchromophores ($\beta = 31 \times 10^{-30}$ esu). Such an enhancement was rationalized by considering metal-to-ligand or ligand-to-metal-to-ligand charge-transfers (CT). Despite these early suggestive results, however, no experimental information is available for the phosphole-based stilbene-type NLO chromophores like **1**. This is apparently because of the lack of a convenient method for introducing functionalized vinyl groups at the α position of the phosphole ring.

To our knowledge, there are only two examples for α-vinylphospholes, both of which were prepared via several steps starting from 3,4-dimethyl-1-phenylphosphole.[6] Recently, Tomita[7] and we[8] independently reported a convenient method for the synthesis of 2,5-disubstituted phospholes via titanacyclopentadiene intermediates. Synthetically, it is of particular interest that the α-ester functions are compatible with the reaction conditions employed.[8] We expected that a similar methodology would be applicable to the introduction of functionalized vinyl groups to the α position of the phosphole ring. Herein, we report the synthesis, structure, and optical properties of unsymmetrically 2,5-disubstituted phospholes bearing an aryl group at one side and a styryl group at the other side. Hyper-Rayleigh scattering experiments on the D−π−A type of 2-aryl-5-styrylphospholes have disclosed that the stilbene-type phosphole derivatives are promising candidates as a new class of second-order NLO chromophores.

Results and Discussion

Synthesis and Characterization of 2-Aryl-5-styrylphospholes. 1,9-Diarylnona-8-ene-1,6-diynes **4a−i**, the precursors of 2-aryl-5-styrylphospholes, were prepared by sequential Sonogashira/Sonogashira coupling or Sonogashira/Negishi coupling reactions of 1,6-heptadiyne with the corresponding iodoarenes and β-bromostyrenes via monosubstituted diynes **3a,b** or enediynes **3c**,**d** (Scheme 1). In the synthesis of **4a−h**, (*E*)-

---

(2) For example, see: (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.; Nyulászi, 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) Hay, C.; Sauthier, M.; Deborde, V.; Hissler, M.; Toupet, L.; Réau, R. *J. Organomet. Chem.* **2002**, *643−644*, 494. (f) Delaere, D.; Nguyen, M. T.; Vanquickenborne, L. G. *J. Phys. Chem. A* **2003**, *107*, 838. (g) Hay, C.; Fave, C.; Hissler, M.; Rault-Berthelot, J.; Réau, R. *Org. Lett.* **2003**, *5*, 3467. (h) Hissler, M.; Rescop, C; Réau, R. *J. Organomet. Chem.* **2005**, *690*, 2482. (i) 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. (j) Baumgartner, T.; Réau, R. *Chem. Rev*. **2006**, *106*, 4681 (*Correction*: **2007**, *107*, 303), and references therein.

(3) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc*. **1997**, *119*, 6575.

(4) The β_x values ($\times$ 10^{-30} esu) of **1a** and **1b** were evaluated using the INDO/1 Hamiltonian to be 45.90 and 39.24, respectively, at the AM1 optimized structures. See ref 3.

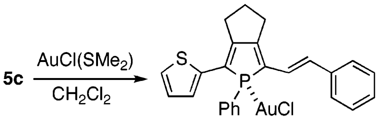
(5) Fave, C.; Hissler, M.; Sénéchal, K.; Ledoux, I.; Zyss, J.; Réau, R. *Chem. Commun*. **2002**, 1674.

(6) (a) Deschamps, E.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun*. **1995**, 1561. (b) Niemi, T.-A.; Coe, P. L.; Till, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1519.

(7) Tomita reported the synthesis of phosphole-containing polymers via titanacyclopentadienes, generated from diethynylbenzene and the Ti(II) reagent. See: (a) Tomita, I.; Ueda, M. *Macromol. Symp*. **2004**, *209*, 217. (b) Tomita, I. *Polym. Prep*. **2004**, *45*, 415.

(8) Matano, Y.; Miyajima, T.; Nakabuchi, T.; Matsutani, Y.; Imahori, H. *J. Org. Chem*. **2006**, *71*, 5792.

isomers were isolated exclusively, irrespective of the stereochemistry of β-bromostyrenes. Reaction of **4a**−**i** 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, Urabe, and co-workers,[9] followed by treatment with dichloro(phenyl)phosphine, afforded 2-aryl-5-styrylphospholes **5a**−**i** in 58−66% isolated yields (Table 1). Note that the ester function in **4f**,**h** and **5f**,**h** is compatible with the reaction conditions employed. The present titanacycle method is highly convenient in that the desired phospholes are readily accessible from commercially available substrates in a few steps.[10] The σ^3-phosphole **5c** smoothly underwent complexation with AuCl(SMe$_2$) to give Au(I)−phosphole complex **6** in 89% yield (eq 1).



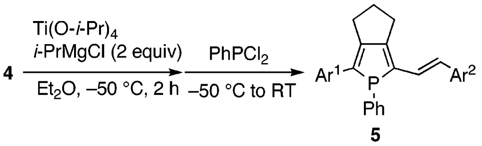
6 (89%)

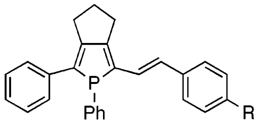
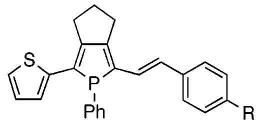
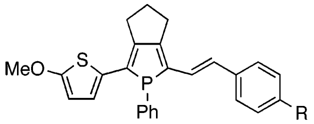
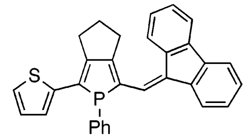
(1)

Phospholes **5a**−**i** and **6** are air stable, yellow or orange solids and have been fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR, MS, and elemental analysis. In the ^{1}H NMR spectra, vinyl protons α to the phosphole ring of **5a**−**h** were observed at δ 6.97−7.11 with relatively large $^3J_{\mathrm{H-P}}$ values of 15.6−16.0 Hz, whereas those β to the phosphole ring of **5a**−**h** were observed at δ 6.53−6.65 with no detectable ^{1}H−^{31}P coupling. The large ^{1}H−^{1}H coupling constants between the two vinyl protons (J = 15.6−16.0 Hz) of **5a**−**h** definitely support the (*E*)-stereochemistry of the styryl groups. The σ^3-phospholes **5a**−**h** displayed the ^{31}P peaks at δ 27.6−29.6, which are more shielded than those observed for the 3,4-C$_3$-bridged σ^3-phospholes bearing ester functions at the α positions (δ 32.0−33.4).[8] On the other hand, the ^{31}P peak of **5i** was observed at downfield (δ 39.3) as compared to those of **5a**−**h**.

The structure of Au(I) complex **6** was further elucidated by X-ray crystallography.[11] There are two sulfur atom positions due to disorder of the thiophene ring, and the major form is depicted in Figure S1. In both forms, the phosphole, thiophene, and benzene rings are nearly coplanar, implying that the π-conjugation could occur efficiently through the phosphole−vinylene bridge.[12] The Julg index[13] (0.71) calculated for the phosphole ring in **6** is comparable to that (0.72) of a structurally characterized 2,5-bis(ethoxycarbonyl)phosphole containing the same five-membered backbone.[8] The phosphorus center adopts a distorted tetrahedral geometry with C−P−C bond angles of 93.40(16)−107.69(13)° and Au−P−C bond angles of 111.82(7)−118.29(13)°. The Au−P bond length [2.2351(7) Å] and the P−Au−Cl bond angle [171.08(4)°] are close to the corresponding values reported for Au(I)−phosphole (monophosphine) complexes.[14]

TABLE 1. Synthesis of 5a−i



entry	endiyne **4**	phosphole **5** (Yield/%)
		
1	**4a**	**5a** (R = H; 63%)
2	**4b**	**5b** (R = CF$_3$; 58%)
		
3	**4c**	**5c** (R = H; 62%)
4	**4d**	**5d** (R = Cl; 65%)
5	**4e**	**5e** (R = CF$_3$; 66%)
6	**4f**	**5f** (R = CO$_2$Me; 59%)
		
7	**4g**	**5g** (R = CF$_3$; 58%)
8	**4h**	**5h** (R = CO$_2$Me; 60%)
		
9	**4i**	**5i** (61%)

Optical Properties of 2-Aryl-5-styrylphospholes. To examine the substituent effects on the optical properties of 2-aryl-5-styrylphospholes, we first measured UV−vis absorption and fluorescence spectra of **5a**−**i** and **6** in THF. The results are summarized in Table 2 and Figure 2. The absorption maxima due to the π−π^* transition of the extended π-conjugated system of 2-thienyl-5-styrylphospholes **5c**,**e** are red-shifted ($\Delta\lambda_{\max}$ = 15−16 nm) relative to those of 2-phenyl-5-styrylphospholes **5a**,**b** with the same *para* substituents. Introduction of a methoxy group at the α position of the thienyl ring and/or introduction of an electron-withdrawing substituent at the *para* position of the benzene ring of the styryl group causes further red-shifts of the absorption maxima ($\Delta\lambda_{\max}$ = 20−22 nm, **5g**,**h** vs **5e**,**f**; $\Delta\lambda_{\max}$ = 4−11 nm, **5e**,**f** vs **5c**). These results suggest that the push−pull (D−A) effect between the two terminal aryl groups operates efficiently through the phosphole−vinylene bridge. The fluorenyl derivative **5i** shows a red-shifted π− π^* transition ($\lambda_{\max}$

---

[9] (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. (c) Sato, F.; Urabe, H.; Okamoto, S. *Pure Appl. Chem.* **1999**, *71*, 1511. (d) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835. (e) Mikami, K.; Matsumoto, Y.; Shiono, T. *Sci. Synth.* **2003**, *2*, 457, and references therein.

[10] Functionalized β-bromostyrenes and 9-(bromomethylene)-9*H*-fluorene were prepared from the corresponding aromatic aldehydes and 9-fluorenone, respectively, in two steps.

[11] Formula C$_{25}$H$_{21}$AuClPS, space group *C2/c*, a = 23.149(3) Å, b = 12.4217(11) Å, c = 18.529(2) Å, β = 125.6476(4)°, V = 4329.7(8) Å^3, Z = 8, D_c = 1.893 g cm^{-3}, 4922 observed and 263 variables, R_w = 0.0482, R = 0.0212 ($I > 2.00\sigma(I)$), GOF = 1.070.

[12] The thiophene and benzene rings are slightly twisted from the phosphole ring with dihedral angles of 4.2° and 7.3°, respectively.

[13] (a) Julg, A.; François, P. *Theor. Chim. Acta (Berlin)* **1967**, *7*, 249. (b) Schleyer, P. V. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337.

[14] (a) Attar, S.; Bearden, W. H.; Alcock, N. W.; Alyea, E. C.; Nelson, J. H. *Inorg. Chem.* **1990**, *29*, 425. Au−P, 2.220(9)−2.227(2) Å; P−Au−Cl, 172.4(1)−178.8(1)°. (b) See ref 2i. Au−P, 2.2290(16)−2.2300(16) Å; P−Au−Cl, 171.64(7)−174.63(8)°. (c) Dienes, Y.; Eggenstein, M.; Neumann, T.; Englert, U.; Baumgartner, T. *Dalton Trans.* **2006**, 1424. Au−P, 2.2249(12) Å; P−Au−Cl, 177.26(4)°.

TABLE 2. Absorption and Fluorescence Maxima of 5-Alkenyl-2-arylphospholes[a]

phosphole	λ_{max}, nm (log ϵ)	λ_{em}, nm[b] (ϕ_f/%[c])	Stokes shift, cm^{-1}
5a	402 (4.40)	490 (2.9)	4.47×10^3
5b	405 (4.44)	504 (0.20)	4.85×10^3
5c	417 (4.43)	516 (4.3)	4.60×10^3
5d	420 (4.49)	522 (2.3)	4.65×10^3
5e	421 (4.48)	545 (0.27)	5.40×10^3
5f	428 (4.52)	552 (0.25)	5.25×10^3
5g	441 (4.49)	613 (0.17)	6.36×10^3
5h	450 (4.56)	622 (0.13)	6.15×10^3
5i	437 (4.35)	*d*	
6	435 (4.35)	555 (3.8)	4.97×10^3

[a] Measured in THF at 25 °C. [b] Excited at 420 nm. [c] Fluorescence quantum yields relative to quinine sulfate. [d] No emission was detected.

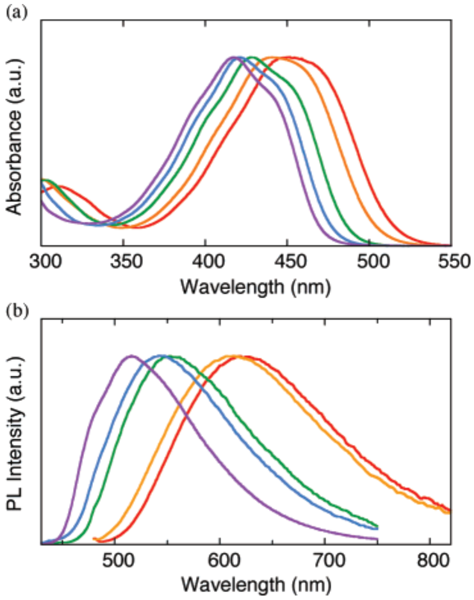


FIGURE 2. UV−vis absorption spectra (a) and fluorescence spectra (b) of **5c**,**e**−**h** in THF. The peak maxima are normalized. The color: **5c**, purple; **5e**, blue; **5f**, green; **5g**, orange; **5h**, red.

= 437 nm) with a lower extinction coefficient (log ϵ = 4.35) as compared to the styryl derivative **5c**. The functionalization at phosphorus from σ^3 to σ^4 also causes a red-shift of the absorption maximum ($\Delta\lambda_{max}$ = 18 nm, **6** vs **5c**). The spectral shapes of **5i** and **6** are slightly different from those of **5a**−**h** (Figure S2), implying that the character of the vibronic states of the 2-aryl-5-styrylphosphole derivatives varies depending on the structure of the vinylene moiety and the electronic property of the phosphorus center.

2-Aryl-5-styrylphospholes **5a**−**i** and **6** are weakly fluorescent, exhibiting emission bands at 490−622 nm with fluorescence quantum yields of 0.13−4.3% in THF. With increasing the electron-withdrawing ability of the *para* substituents of the styryl group and/or the electron-donating ability of the thienyl group, the emission maxima (λ_{em}) are shifted to longer wavelengths. For instance, the λ_{em} value increases in the order: 2-(2-thienyl)-5-styrylphosphole **5c** (516 nm) < 2-(2-thienyl)-5-(4-methoxycarbonylstyryl)phosphole **5f** (552 nm) < 2-(5-methoxy-2-thienyl)-5-(4-methoxycarbonylstyryl)phosphole **5h** (622 nm). As shown in Table 2, the degree of bathochromic shift of λ_{em} is considerably larger than that of λ_{max}, indicating that the CT interaction in the excited-state is more pronounced than that in the ground state. It is apparent that the π-conjugative CT interaction between the electron-donating thienyl group and the electron-withdrawing phenyl group plays a crucial role in controlling the HOMO−LUMO gap.

To get further insight into the substituent effects on the polarizability of the π-conjugated system in 2-aryl-5-styrylphospholes, we next examined solvatochromism of absorption and fluorescence spectra of **5c**,**e**−**h** and **6** using nine solvents with different polarity (Table S1). When the solvent was changed from nonpolar cyclohexane to polar *N*,*N*-dimethylformamide (DMF), the emission maximum of **5c** exhibited larger bathochromic shift ($\Delta\lambda_{em}$ = 14 nm) than the absorption maximum ($\Delta\lambda_{max}$ = 3 nm). As shown in Figure S3, a Kamlet−Taft analysis[15] for the fluorescence spectra of **5c** gave a linear solvation energy relationship (LSER) vs the solvatochromic parameter π^* [$\nu_{em} = 19.68 - 0.56\pi^*$ (10^3 cm^{-1})] with an *R* value of 0.952 (*n* = 9). On the contrary, a reliable LSER could not be given from the absorption spectra, due to little difference in their λ_{max} values. It is most likely that the polarizability of the excited-state of **5c** is more significant than that of the ground state. Similarly, **5e**−**h** and **6** showed appreciable solvatochromism in their fluorescence spectra (Figure S3), displaying the following LSERs: **5e** [$\nu_{em} = 19.09 - 1.10\pi^*$ (10^3 cm^{-1}); *R* = 0.937 (*n* = 9)]; **5f** [$\nu_{em} = 18.96 - 1.65\pi^*$ (10^3 cm^{-1}); *R* = 0.954 (*n* = 9)]; **5g** [$\nu_{em} = 17.42 - 1.76\pi^*$ (10^3 cm^{-1}); *R* = 0.956 (*n* = 9)]; **5h** [$\nu_{em} = 17.18 - 1.98\pi^*$ (10^3 cm^{-1}); *R* = 0.964 (*n* = 9)]; **6** [$\nu_{em} = 18.46 - 0.91\pi^*$ (10^3 cm^{-1}); *R* = 0.967 (*n* = 9)]. Thus, the slope of LSER increases in the order **5c** < **6** < **5e** < **5f** < **5g** < **5h**, indicating that both the electron-withdrawing *para* substituents of the styryl group and the electron-donating α substituent of the thienyl group are indispensable for providing high polarizability in the excited state. It has been clarified that the combination of 5-methoxy-2-thienyl and 4-methoxycarbonylphenyl groups is best for the polarization of the phosphole−vinylene-bridged π-conjugated system.

NLO Properties of 2-Aryl-5-styrylphospholes. One of the promising approaches to construct efficient second-order NLO chromophores is to attach electron donor and electron acceptor substituents at the opposite ends of a suitable π-conjugated bridge.[16] Namely, the larger the difference in dipole moments between the ground state and the excited-state of the π-conjugated system is, the higher the performance of the NLO chromophore becomes. To systematically evaluate the NLO response properties of the 2-aryl-5-styrylphospholes at the molecular level, we finally measured the first molecular hyperpolarizabilities (β) of **5e**−**h** in dioxane using the hyper-Rayleigh scattering (HRS) method[17] at a fundamental wavelength of a Nd:YAG laser (1064 nm).[18] Although our samples are weakly fluorescent, the effect of two-photon excitation[19] was well removed by using a multichannel detector as is described in the experimental section.[18] The β values were

---

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

(16) For example, see: (a) *Molecular Nonlinear Optics: Materials, Physics and Devices*; Zyss, J., Ed.; Academic Press: Boston, 1993. (b) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987. (c) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (d) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994,** *94*, 195. (e) Cariati, E.; Pizzotti, M.; Roberto, D.; Tessore, F.; Ugo, R. *Coord. Chem. Rev.* **2006**, *250*, 1210. (f) Maury, O.; Le Bozec, H. *Acc. Chem. Res.* **2005**, *38*, 691.

(17) (a) Clays, K.; Perssoons, A. *Rev. Sci. Instrum.* **1992**, *63*, 3285. (b) Clays, K.; Perssoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980.

(18) The details of the HRS measurements for **5e**−**h** are provided in the Experimental Section.

TABLE 3. Nonlinear Optical Data of 2-Aryl-5-styrylphospholes

phosphole	$\beta_{1064}{}^{a}$ ($\beta_{1907}{}^{b}$), ($\times 10^{-30}$ esu)
5e	44 (18)
5f	79 (30)
5g	129 (45)
5h	204 (66)

[a] Obtained by the HRS method in dioxane. The estimated errors are ca. 10% of the values. [b] Calculated using the two-level model.

determined by the external reference method against *p*-nitroaniline (PNA) and are summarized in Table 3.[20] On the basis of a simple two-level model,[21] we estimate hyperpolarizabilities of **5e**−**h** at 1.91 μm as 18 (**5e**), 30 (**5f**), 45 (**5g**), and 66 (**5h**). Although care must be taken for evaluating these calculated values,[22] it is likely that the NLO response properties of the D−π−A type of 2-aryl-5-styrylphospholes **5g**,**h** are large according to the classifications proposed by Marks and coworkers.[16d] The 2-thienyl-5-styrylphospholes **5e**,**f** bearing an electron-withdrawing substituent at the *para* position of the phenyl group showed moderate NLO responses ($\beta = 44 \times 10^{-30}$ and 79×10^{-30} esu), which are 2.6−4.6 times greater than that of PNA ($\beta = 16.9 \times 10^{-30}$ esu). The 2-(5-methoxy-2-thienyl)-5-styrylphospholes **5g**,**h** exhibit larger NLO responses ($\beta = 129 \times 10^{-30}$ and 204×10^{-30} esu) than the corresponding α-free thienyl derivatives **5e**,**f**. Thus, introduction of the methoxy group at the α position of the thiophene ring enhances the NLO response property largely. These data represent that the resonance/inductive effects derived from the electron-donating and electron-withdrawing substituents at the termini operate effectively in hyperpolarization through the phosphole−vinylene bridged π-conjugated system.

Conclusions

We have established a reliable route for the synthesis of 2-aryl-5-styrylphospholes from 1,9-diarylnona-8-ene-1,6-diynes and dichloro(phenyl)phosphine via intermediary titanacyclopentadienes. The observed optical properties of the push−pull type of derivatives represent that the charge−transfer interaction between the two terminal aryl groups dramatically affect the polarizability of the phosphole−vinylene-bridged π-conjugated system. Among the newly prepared phospholes, 2-(5-methoxy-2-thienyl)-5-[4-(methoxycarbonyl)styryl]phosphole exhibits the highest molecular hyperpolarizability, which exemplifies the potential utility of this class of phosphole derivatives as promising candidates for efficient second-order NLO chromophores.

Experimental Section

Synthesis of 2-Aryl-5-styrylphospholes. Typical Procedure. To a mixture of **4a** (270 mg, 1.0 mmol), Ti(O-*i*-Pr)$_4$ (0.29 mL, 1.0 mmol), and Et$_2$O (15 mL) was slowly added an ether solution of *i*-PrMgCl (2.0 M × 1.0 mL, 2.0 mmol) at −78 °C, and the resulting mixture was stirred for 2 h at −50 °C. Dichloro(phenyl)phosphine (0.14 mL, 1.0 mmol) was then added to the mixture at this temperature, and the resulting suspension was allowed to warm to 0 °C and stirred for 1 h at this temperature. After stirring for an additional 2 h at room temperature, a saturated aq NH$_4$Cl solution (10 mL) was poured into the reaction mixture, and insoluble substances were filtered off through a Celite bed. The Celite bed was washed with AcOEt repeatedly, and the filtrate was washed with brine (50 mL). The aqueous phase was extracted with AcOEt (20 mL × 2), and the combined organic extracts were dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The solid residue was subjected to short silica gel column chromatography (CH$_2$Cl$_2$). The yellow fraction was collected and evaporated to give a yellowish solid, which was then washed with MeOH. 2-Phenyl-5-styrylphosphole **5a** was isolated as a yellow solid (240 mg, 63%). Mp 161−162 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.35 (tt, 2H, J = 7.2, 7.2 Hz), 2.57−2.87 (m, 3H), 2.92−3.05 (m, 1H), 6.65 (d, 1H, J = 15.6 Hz), 7.03 (dd, 1H, J = 15.6 Hz, ^3J(P,H) = 15.6 Hz), 7.08−7.18 (m, 2H), 7.20−7.30 (m, 7H), 7.27−7.37 (m, 2H), 7.42−7.50 (m, 4H); ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz) δ 27.0 (d, $J_{\mathrm{P-C}}$ = 1.3 Hz), 29.2, 29.3 (d, $J_{\mathrm{P-C}}$ = 1.3 Hz), 123.6 (d, $J_{\mathrm{P-C}}$ = 17.4 Hz), 126.2, 126.2 (d, $J_{\mathrm{P-C}}$ = 1.3 Hz), 127.1, 127.5 (d, $J_{\mathrm{P-C}}$ = 9.9 Hz), 128.4, 128.5, 128.7 (d, $J_{\mathrm{P-C}}$ = 8.1 Hz), 129.3 (d, $J_{\mathrm{P-C}}$ = 1.9 Hz), 129.4 (d, $J_{\mathrm{P-C}}$ = 10.6 Hz), 133.3 (d, $J_{\mathrm{P-C}}$ = 18.7 Hz), 133.6 (d, $J_{\mathrm{P-C}}$ = 11.8 Hz), 136.2, 136.9 (d, $J_{\mathrm{P-C}}$ = 18.7 Hz), 137.2, 137.8, 154.2 (d, $J_{\mathrm{P-C}}$ = 9.4 Hz), 157.8 (d, $J_{\mathrm{P-C}}$ = 8.7 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz) δ + 27.7; UV/vis (THF) $\lambda_{\max}$ (ϵ) 402 (25300); Fluorescence (THF) λ_{em}(ϕ_{f}/%) 490 (2.9); MS (MALDI-TOF) *m*/*z* 378 (M$^+$); Anal. Calcd for C$_{27}$H$_{23}$P: C, 85.69; H, 6.13. Found: C, 85.56; H, 6.12.

Synthesis of Au(I) Complex 6. A mixture of **5c** (38 mg, 0.10 mmol), AuCl(SMe$_2$) (32 mg, 0.11 mmol), and CH$_2$Cl$_2$ (10 mL) was stirred for 1 h at room temperature. The mixture was then concentrated under reduced pressure and subjected to short silica gel column chromatography (CH$_2$Cl$_2$). The first yellow fraction was collected and washed with MeOH to give **5** as an orange solid (55 mg, 89%). Mp 220 °C (dec); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.32−2.53 (m, 2H), 2.75−3.00 (m, 4H), 6.80−6.96 (m, 3H), 7.19−7.35 (m, 7H), 7.40−7.55 (m, 3H), 7.76−7.83 (m, 2H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) δ 27.8 (d, $J_{\mathrm{P-C}}$ = 8.8 Hz), 28.0 (d, $J_{\mathrm{P-C}}$ = 1.3 Hz), 29.9 (d, $J_{\mathrm{P-C}}$ = 8.1 Hz), 120.1 (d, $J_{\mathrm{P-C}}$ = 14.9 Hz), 122.3, 123.2, 125.9 (d, $J_{\mathrm{P-C}}$ = 2.5 Hz), 126.6, 126.7 (d, $J_{\mathrm{P-C}}$ = 1.9 Hz), 128.0, 128.3, 128.7, 129.6 (d, $J_{\mathrm{P-C}}$ = 11.2 Hz), 132.5 (d, $J_{\mathrm{P-C}}$ = 8.1 Hz), 132.8 (d, $J_{\mathrm{P-C}}$ = 2.5 Hz), 133.8 (d, $J_{\mathrm{P-C}}$ = 14.3 Hz), 136.4 (d, $J_{\mathrm{P-C}}$ = 20.5 Hz), 136.5, 155.9 (d, $J_{\mathrm{P-C}}$ = 15.5 Hz), 160.4 (d, $J_{\mathrm{P-C}}$ = 16.1 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz) δ + 52.4; UV/vis (THF) $\lambda_{\max}$ (ϵ) 435 (22400); Fluorescence (THF) λ_{em}(ϕ_{f}/%) 555 (3.8); MS (MALDI-TOF) *m*/*z* 617 (M$^+$).

Hyper-Rayleigh Light Scattering (HRS) Measurements. The first hyperpolarizabilities (β) of 2-aryl-5-styrylphospholes were determined using the hyper-Rayleigh light scattering (HRS) method using a fundamental output (1064 nm) from a Nd:YAG laser (10 Hz, ca. 5−7 ns). The beam at a fundamental wavelength (1064 nm) was focused in the solution in a 1 cm glass cell with a beam diameter of ca. 1.6 mm by a lens with a focal length of 200 mm. The hyper-Rayleigh signal from the solution was collected at a 90° scattering geometry and focused on a slit of a 64 cm monochromator

---

(19) (a) Flipse, M. C.; de Jonge, R.; Woudenberg, R. H.; Marsman, A. W.; van Walree, C. A.; Jenneskens, L. W. *Chem. Phys. Lett.* **1995**, *245*, 297. (b) Song, N. W.; Kang, T.-I.; Jeoung, S. C.; Jeon, S.-J.; Cho, B. R.; Kim, D. *Chem. Phys. Lett.* **1996**, *261*, 307.

(20) The β value of PNA at 1064 nm (dioxane) is reported to be 16.9, which was determined using the electric field induced second harmonic generation (EFISH) method. See: (a) Teng, C. C.; Garito, A. F. *Phys. Rev. B* **1983**, *28*, 6766. (b) Stähelin, M.; Burland, D. M.; Rice, J. E. *Chem. Phys. Lett.* **1992**, *191*, 245.

(21) (a) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664. (b) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446. (c) Oudar, J. L.; Zyss, J. *Phys. Rev. A* **1982**, *26*, 2016. The β values at 1.91 μm were calculated according to the following equation neglecting damping factors: $\beta_{1.91} = \beta_{1.06}(R_{1.06}/R_{1.91})$; $R_{\omega} = \omega_0{}^2/(\omega_0{}^2 - \omega^2)(\omega_0{}^2 - 4\omega^2)$, where ω_0 is the frequency of the absorption maximum.

(22) It has been pointed out that the intrinsic hyperpolarizabilities (β_0) calculated from 1064 nm HRS data somewhat differ from the 1907 nm results. This discrepancy has been attributed to the difficulty of the estimation of the resonance enhancement associated with the 1064 nm radiation employed in the HRS experiments. However, the traditional way (note 21) still gives rough estimations. For example, see: (a) Wang, C. H.; Woodford, J. N.; Jen, A. K.-Y. *Chem. Phys.* **2000**, *262*, 475. (b) Clays, K.; Hendrickx, E.; Verbiest, T.; Persoons, A. *Adv. Mater.* **1998**, *10*, 643. (c) Wolff, J. J.; Wortmann, R. *Adv. Phys. Org. Chem.* **1999**, 121.

(a 1800 lines/mm grating) equipped with a CCD camera (1340 × 400 imaging pixels, 20 × 20-μm pixels). The hyper-Rayleigh signal detected at 532 nm was easily resolved from other background signals (e.g., two-photon fluorescence) by using a multichannel detector, since the signal appears as a strong spike over the smooth background. It was ensured that the hyper-Rayleigh signal was proportional to the square of the laser pulse energy at least up to ca. 25 mJ. In the determination of β, the concentration dependence of the hyper-Rayleigh signal intensity was measured at the fixed pulse energy (ca. 20 mJ). Freshly distilled dioxane was used as a solvent, and the β values of **5e**−**h** were measured using the external reference method against a standard solution of *p*-nitroaniline (PNA) in the same solvent: the relative hyperpolarizabilities of two chromophores are given by $\beta = \beta_{\mathrm{ref}} \times (m/m_{\mathrm{ref}})^{1/2}$, where m is slope of the hyper-Rayleigh signal intensity against the solute concentration. The concentrations of PNA were less than 14 mM, and those of **5e,f** were less than 1 mM. In the measurements of **5g**,**h**, the diluted sample solutions (<0.1 mM) were used to avoid self-absorption of the second harmonic generation signal at 532 nm, and the effect of the reabsorption was corrected.

Acknowledgment. This work was partially supported by a Grant-in-Aid (No. 19027030) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Supporting Information Available: Experimental details, synthetic procedures and characterization data for **3a**−**d**, **4a**−**i**, and **5b**−**i**, ^{1}H NMR charts for new compounds, and CIF file for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO070822F