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Synthesis and Redox Properties of Sterically Crowded Triarylphosphine and Tetraaryldiphosphane Bearing Phenothiazinyl Groups

Shigeru Sasaki, Midori Murakami, Fumiki Murakami, and Masaaki Yoshifuji

Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aoba, Aoba-ku, Sendai 980-8578, Japan

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ABSTRACT: *Sterically crowded triarylphosphines and tetraaryldiphosphane bearing phenothiazinyl groups as redox sites were synthesized by using 2-bromo-1,3-dialkyl-5-phenothiazinylbenzenes as key synthetic intermediates. Cyclic voltammograms of these compounds show the first redox wave corresponding to the oxidation of the phosphorus redox center and the following waves corresponding to the oxidation of the phenothiazinyl groups. Introduction of more sterically crowded triarylphosphine moiety leads to more reversible oxidation of the phosphine as well as the phenothiazine moieties. A crowded tetraaryldiphosphane bearing four phenothiazinyl groups are oxidized in two steps. Four phenothiazine moieties are oxidized nearly at once after oxidation of the diphosphane moiety.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:506–513, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20714

Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

Correspondence to: Shigeru Sasaki; e-mail: ssasaki@m.tohoku.ac.jp.

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INTRODUCTION

Sterically crowded triarylphosphines and tetraaryldiphosphanes are known to be oxidized reversibly to give persistent radical cations [1]. Representative compounds are 2,4,6-trimethylphenyl derivatives **1a** [2] and **2a** [3], and 2,4,6-triisopropylphenyl derivatives **1b** [4] and **2b** [5] (Chart 1). We synthesized crowded triarylphosphines and arsines having structure around pnictogen similar to **1a**, bearing amino and phenothiazinyl groups [6]. However, even with the help of the stability of phenothiazinylbenzene redox cycle [7], triarylphosphines such as **3a** were reversibly oxidized in two steps only at low temperature (Chart 2). Tris(2,4,6-triisopropylphenyl)phosphine (**1b**) and the related compounds are reported to give more stable redox systems as well as radical cations [4], and we have synthesized crowded triarylphosphines structurally similar to **1b**, bearing various functional sites such as donors [8], acceptors [9], and radicals [10]. The electrochemical measurement of these functionalized crowded triarylphosphines showed that the phosphine moieties worked as reversible redox sites and the molecules as a whole became multistep reversible redox systems. Herein we report synthesis and redox properties of sterically crowded triarylphosphines **3b** and **3c** bearing phenothiazinyl groups [11]. Enhanced stability of the phosphorus

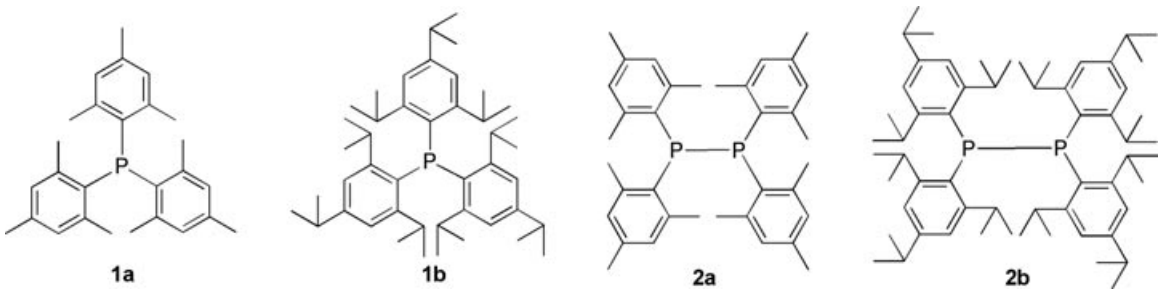


CHART 1

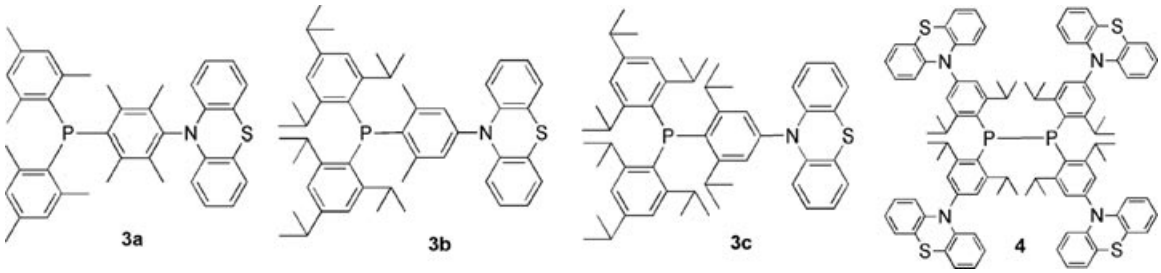


CHART 2

redox center contributes to the stability of the whole redox systems. Tetraaryldiphosphane **4** bearing four phenothiazinyl groups was also synthesized and redox properties were revealed.

RESULTS AND DISCUSSION

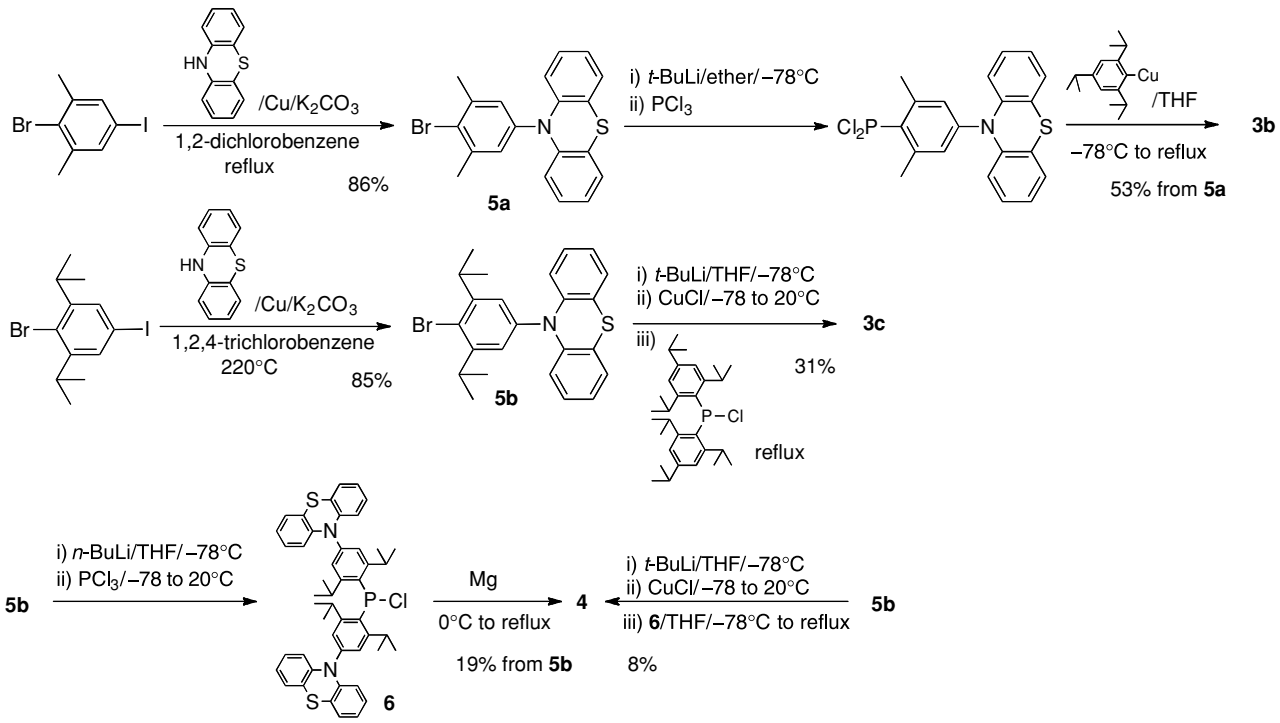
Synthesis and Structure

Key synthetic intermediates, 2-bromo-1,3-dimethyl-5-phenothiazinylbenzene (**5a**) and 2-bromo-1,3-diisopropyl-5-phenothiazinylbenzene (**5b**), were synthesized from 2-bromo-1,3-dialkyl-5-iodoobenzenes [8] by Ullmann coupling (Scheme 1). Bromobenzene **5a** was converted to the corresponding aryldichlorophosphine and was reacted with 2,4,6-triisopropylphenylcopper(I) [12] to give **3b**. On the other hand, bromobenzene **5b** was converted to the corresponding arylcopper(I) reagent and was coupled with chlorobis(2,4,6-triisopropylphenyl)phosphine [13] to give triarylphosphine **3c**. The lithiation of **5b** followed by the reaction with a half equivalent of phosphorus trichloride gave chlorophosphine **6**. Attempted synthesis of the triarylphosphine bearing three phenothiazinylaryl groups was unsuccessful and tetraaryldiphosphane **4** was obtained instead. Diphosphane **4** was also synthesized by the reductive coupling of **6**.

Triarylphosphines **3b** and **3c** show upfield ^{31}P NMR chemical shift [δ −46.2 (**3b**), −50.1 (**3c**), −36 (**1a**), −52.4 (**1b**)] typical of this kind of crowded triarylphosphines. Diphosphane **4** also shows upfield ^{31}P NMR chemical shift similar to the related compounds [δ −35.7, −40.1 (**2b**)]. The substituents on the phosphorus of **3c** exhibit inversion-averaged ^{1}H and ^{13}C NMR spectra typical of the phosphines similar to **1b**. As a result of the rapid inversion, triarylphosphine **3c**, in which one aryl group is different among three, gives the three different aryl groups at 296 K. The ^{1}H and ^{13}C NMR spectra of diphosphane **4** also reflect the crowded structure around the phosphorus, where nonequivalent four methine and eight methyl groups are observed. Diphosphane **4** shows downfield methine protons and AA′XX′ patterns of ^{13}C signals similar to **2b** [5].

Redox Properties

The redox properties of **3b, 3c**, and **4** were studied by cyclic voltammetry. In spite of the introduction of two 2,4,6-triisopropylphenyl groups, redox waves of **3b** are irreversible even at 195 K (Fig. 1). Less sterically crowded **3a** exhibits nearly reversible waves under similar conditions [6]. On the other hand, **3c** shows reversible two-step redox waves followed by irreversible waves at 295 K (Fig. 2). The introduction of the phosphorus redox center similar to **1b** contributes to the stabilization of the whole redox



SCHEME 1 Synthesis of sterically crowded triarylphosphines and tetraaryldiphosphane bearing phenothiazines.

systems as compared with **3a** and **3b**. Judging from comparison with the oxidation potentials of each subunit [$^1E_{1/2}$ = 0.16 V (**1b**), 0.48 V (**5b**)], the first oxidation takes place on the phosphorus followed by the second oxidation on the nitrogen. The introduction of a phenothiazinyl group in place of an isopropyl group raises the oxidation potential of the phosphines as seen in trimethylphenyl derivatives [6]. Diphosphane **4** gave the first quasi-reversible oxidation followed by one-step (unresolved) intense reversible wave (Fig. 3). The first oxidation is deduced to take place on the diphosphane moiety, judging from comparison with the oxidation potential of similar compounds [$^1E_{1/2}$ = 0.04 (**2b**), 0.48 (**5b**) V] and electron withdrawing effect of the phenothiazinyl groups as compared with isopropyl groups as shown above. Delocalization of the positive charge to the two phosphorus atoms relieves positive charge repulsion among charges on the phenothiazines and the phosphorus atoms.

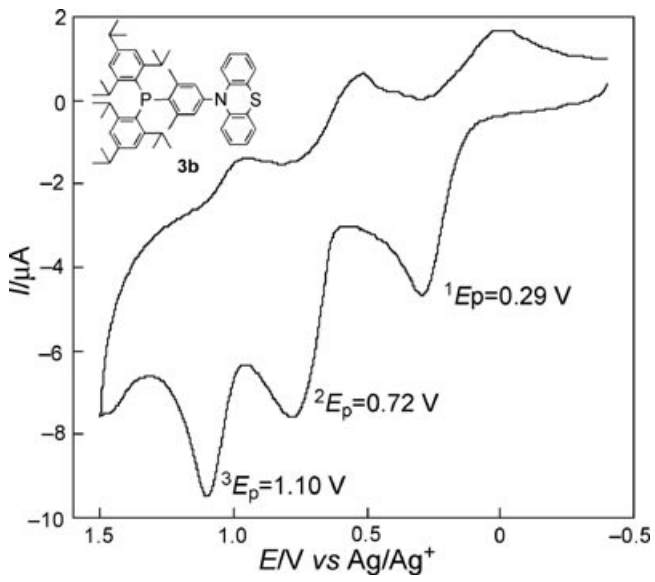


FIGURE 1 Cyclic voltammogram of **3b** at 195 K. Scan rate 50 mV s^{-1}.

In order to get further insight into the oxidation of the triarylphosphines bearing phenothiazines, electron paramagnetic resonance (EPR) study of the oxidation was carried out. Phosphine **3b** can be chemically oxidized by tris(4-bromophenyl)aminium perchlorate in dichloromethane to give yellow-brown solution. Phosphine **3c** can be oxidized by various reagents such as tris(4-bromophenyl)aminium perchlorate and silver(I) perchlorate in dichloromethane to give brown solution. The EPR spectra of both solutions

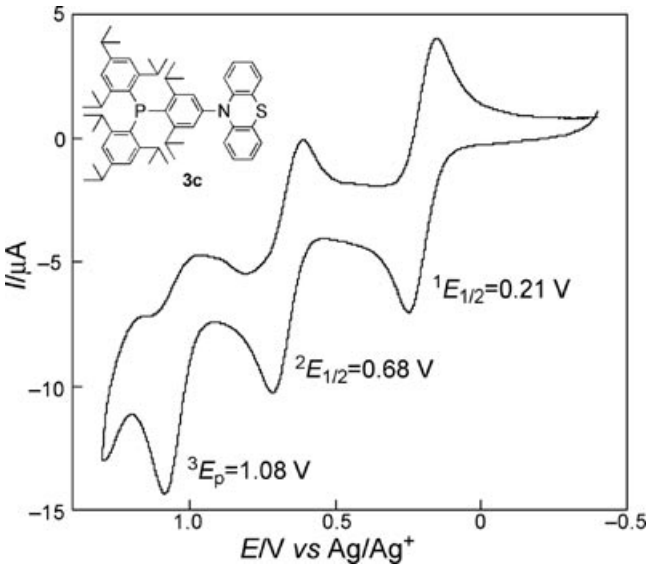


FIGURE 2 Cyclic voltammogram of **3c** at 295 K. Scan rate 30 mV s^{-1}.

consist of two lines typical of the radical cations of the sterically crowded triarylphosphines and the corresponding frozen solutions gave the axial symmetrical powder patterns of the hyperfine coupling tensor (Fig. 4). Isotropic and anisotropic hyperfine coupling constants obtained by oxidation of **3c** are very similar to those of **1b** ($g = 2.007$, $a = 23.7$ mT, $g_{//} = 2.002$, $a_{//} = 41.7$ mT, $g_{\perp} = 2.009$, $a_{\perp} = 13.0$ mT), suggesting generation of very similar radical cations. However, the use of an excess

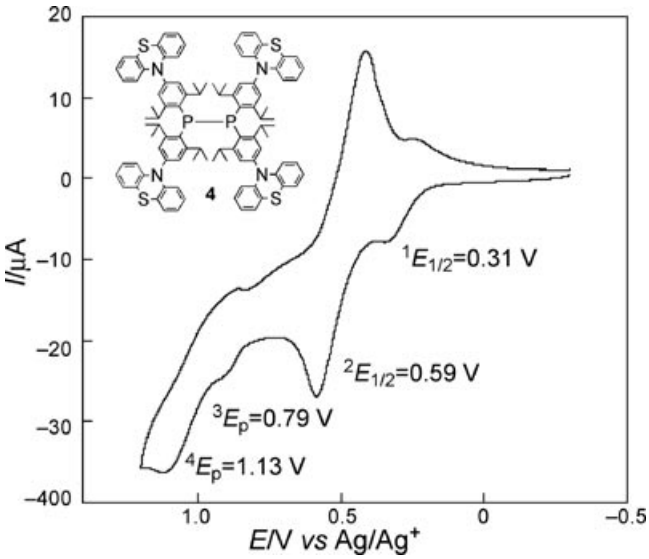


FIGURE 3 Cyclic voltammogram of **4** at 295 K. Scan rate 30 mV s^{-1}.

amount of the oxidant did not give signals other than those of the phosphorus radical cations. Other signals such as the fine structures, $\Delta m_s = 2$ transitions typical of the triplet species, and hyperfine structures of the nitrogen radicals were not observed. The brown color of the solutions, which is different from the typical purple color of the radical cation of triarylphosphine, strongly suggests the intramolecular interaction between the phosphorus radical cation and the phenothiazine, but it is probable that the highly oxidized species are too reactive to allow direct observation rather than the formation of the closed shell species such as **6** (Scheme 2).

CONCLUSION

The redox study on a series of sterically crowded triarylphosphines bearing phenothiazine moieties showed that the development of the stable phosphorus redox centers greatly contributes to the construction of the stable multistep redox systems composed of various redox sites. Although the triarylphosphine redox centers still need marginal stability to overcome instability of the highly oxidized state, this work provides guideline for the construction of the practical redox centers bearing main group elements as key components.

EXPERIMENTAL

^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker (Germany) AM600, AV400, or a JEOL (Tokyo, Japan) JNM-A500 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are expressed as δ downfield from external tetramethylsilane and calibrated to the residual proton of the deuterated solvents (δ 7.26 for chloroform-*d*, 7.27 for benzene-d_6) or the carbon of the deuterated solvent (δ 77.0 for chloroform-*d*, 128.0 for benzene-d_6). ^{31}P NMR chemical shifts are expressed as δ downfield from external 85% H_3PO_4. Mass spectra were measured on a Hitachi (Tokyo, Japan) M-2500S with electron impact (EI) ionization at 70 eV, or a JEOL HX-110 with fast atom bombardment ionization using *m*-nitrobenzyl alcohol matrix. Melting points were measured on a Yanagimoto (Kyoto, Japan) MP-J3 apparatus, without correction. Merck (Darmstadt, Germany) silica gel 60 and Sumitomo (Tokyo, Japan) basic alumina (KCG-30) were used for the column chromatography. All reactions were carried out under argon unless otherwise specified. Anhydrous tetrahydrofuran and ether were distilled from sodium diphenylketyl under argon just prior to use. Cyclic voltammetry was performed on a BAS (West Lafayette, IN) CV-50W controller

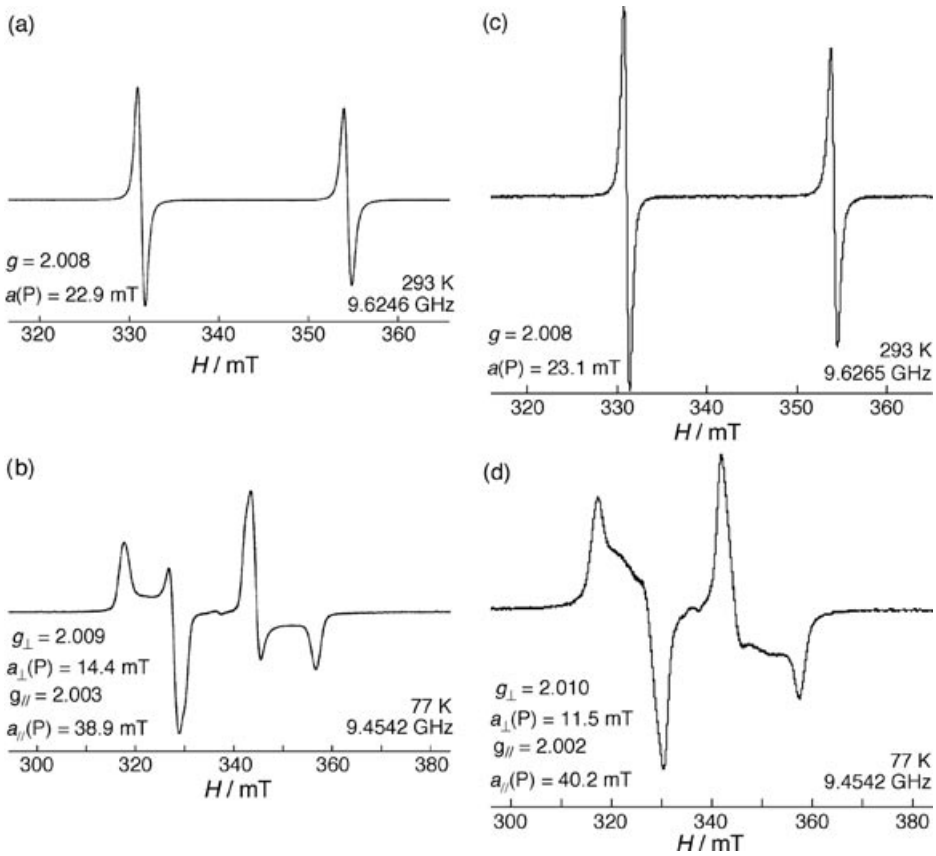
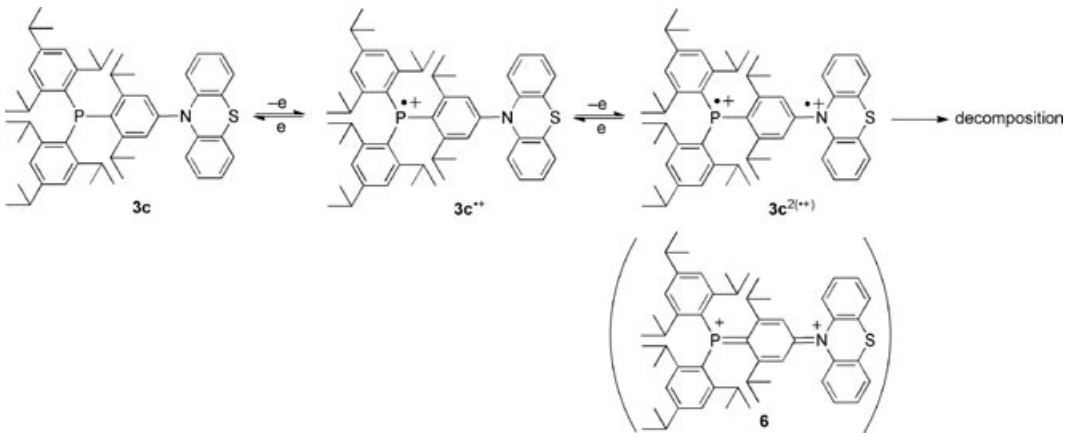


FIGURE 4 EPR spectra obtained after oxidation of (a) **3b** with tris(4-bromophenyl)aminium perchlorate in dichloromethane at 293 K ($g = 2.008$, $a = 22.9$ mT), (b) at 77 K ($g_{//} = 2.003$, $a_{//} = 38.9$ mT, $g_{\perp} = 2.009$, $a_{\perp} = 14.4$ mT), (c) **3c** with silver(I) perchlorate in dichloromethane at 293 K ($g = 2.008$, $a = 23.1$ mT), and (d) at 77 K ($g_{//} = 2.002$, $a_{//} = 40.2$ mT, $g_{\perp} = 2.010$, $a_{\perp} = 11.5$ mT).

with a glassy carbon, Pt wire, and Ag/0.01 mol L^{-1}, $AgNO_3$/0.1 mol L^{-1}, n-Bu_4NClO_4/CH_3CN as a working, counter, and reference electrode, respectively (Ferrocene/Ferricinium = 0.18 V). A substrate (*ca.* 10^{-4} mol L^{-1}) was dissolved in dichloromethane with 0.1 mol L^{-1} n-Bu_4NClO_4 as a supporting electrolyte, and the solution was degassed by bubbling with nitrogen gas. X-band EPR spectra were measured on a Bruker ESP300E spectrometer equipped with a JEOL ES-UCD2X liquid nitrogen Dewar. Samples



SCHEME 2 Redox process of **3c**.

were dissolved in dichloromethane, which was distilled over calcium hydride, degassed by the freeze-and-thaw cycles, and transferred to a sample by bulb-to-bulb distillation. Oxidation was carried out in an H-shaped sealed tube.

*2-Bromo-1,3-dimethyl-5-phenothiazinylbenzene (**5a**)*: A mixture of phenothiazine (100 mg, 0.504 mmol), 2-bromo-1,3-dimethyl-5-iodobenzene (194 mg, 0.625 mmol), potassium carbonate (275 mg, 1.99 mmol), copper powder (66.2 mg, 1.04 mmol), and 1,2-dichlorobenzene (3 mL) was refluxed for 48 h. The mixture was cooled to 20°C and directly submitted to column chromatography (SiO_2, *n*-hexane) to give **5a** (166 mg, 0.434 mmol, 86%). **5a**: colorless needles; mp 200.5–203.0°C; ^{1}H NMR (500 MHz, $CDCl_3$, 296 K): δ 7.12 (2H, s, Ar-4,6), 7.01 (2H, dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, pheno-4,6), 6.90–6.70 (4H, brs, pheno-2,3,7,8), 6.25 (2H, brd, $^3J_{HH}$ = 7.0 Hz, pheno-1,9), 2.49 (6H, s, CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 296 K): δ143.84 (brs, pheno-9a,10a), 141.02 (s, Ar-1,3), 139.25 (brs, Ar-5), 130.13 (brs, Ar-4,6), 127.02 (s, Ar-2), 126.82 (s, pheno-2,8), 126.72 (brs, pheno-4,6), 122.55 (brs, pheno-3,7), 120.26 (brs, pheno-4a,5a), 116.04 (s, pheno-1,9), 24.01 (s, CH_3); LRMS (70 eV, EI) 383 ($M^+ + 2$; 100), 381 (M^+; 95), 302 (M^+−Br).

*2-Bromo-1,3-diisopropyl-5-phenothiazinylbenzene (**5b**)*: A mixture of phenothiazine (2.50g, 12.5 mmol), 2-bromo-1,3-diisopropyl-5-iodobenzene (3.52 g, 9.59 mmol), potassium carbonate (5.67 g, 41.0 mmol), copper powder (1.34 g, 21.1 mmol), and 1,2,4-trichlorobenzene (9 mL) was stirred at 220°C for 40 h. The mixture was cooled to 20°C and directly submitted to column chromatography (SiO_2, *n*-hexane, *n*-hexane/chloroform = 5/1) to give **5b** (3.57 g, 8.15 mmol, 85%). **5b**: pale yellow crystals; mp 175.0–178.0°C; ^{1}H NMR (400 MHz, C_6D_6, 296 K): δ7.17 (2H, s, Ar-4,6), 7.08 (2H, dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.6 Hz, pheno-4,6), 6.78 (2H, td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, pheno-2,8), 6.70 (2H, td, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, pheno-3,7), 6.38 (2H, dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz, pheno-1,9), 3.64 [2H, sept, $^3J_{HH}$ = 6.8 Hz, C$\underline{H}$(CH_3)$_2$], 1.11 [12H, d, $^3J_{HH}$ = 6.9 Hz, CH(C$\underline{H}_3$)$_2$]; $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 296 K): δ 151.49 (s, Ar-1,3), 145.13 (s, pheno-9a,10a), 141.02 (s, Ar-5), 127.50 (s, Ar-2), 127.45 (s, pheno-2,8 or 4,6), 127.41 (s, pheno-2,8 or 4,6), 126.45 (s, Ar-4,6), 123.21 (s, pheno-3,7), 120.86 (s, pheno-4a,5a), 116.19 (s, pheno-1,9), 34.24 [s, C$\underline{H}$(CH_3)$_2$], 23.00 [s, CH(C$\underline{H}_3$)$_2$]; LRMS (70 eV, EI) *m*/*z* (rel intensity) 439 (M^+; 100), 359 (M^+−Br; 23), 198 (Tip; 14).

*(2,6,-Dimethyl-4-phenothiazinylphenyl)bis(2,4,6-triisopropylphenyl)phosphine (**3b**)*: To a solution of **5a** (403 mg, 1.05 mmol) in ether (80 mL), *t*-butyllithium (1.47 mol L^{-1} in pentane, 1.50 mL, 2.21 mmol) was added at −78°C. The solution was stirred for 30 min and then phosphorus trichloride (1.0 mL, 11.5 mmol) was added. The resultant mixture was stirred for 30 min, warmed to room temperature, stirred for 10 h, and concentrated under reduced pressure to give crude dichloro(2,6-dimethyl-4-phenothiazinylphenyl)phosphine. To a solution of 2,4,6-triisopropylphenylmagnesium bromide prepared from 2-bromo-1,3,5-triisopropylbenzene (748 mg, 2.64 mmol), magnesium (68.3 mg, 2.81 mmol), and tetrahydrofuran (5 mL), copper(I) chloride (302 mg, 3.05 mmol) was added at −78°C. The mixture was stirred for 5 min, warmed to 20°C, stirred for 19 h, and cooled to −78°C. To the mixture, a solution of dichloro(2,6-dimethyl-4-phenothiazinylphenyl)phosphine in tetrahydrofuran (30 mL) was added in 10 min. The mixture was stirred for 2 h, warmed, refluxed for 20 h, and cooled to room temperature. *n*-Hexane was added and the resultant suspension was filtered by Celite. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (Al_2O_3, *n*-hexane) to give **3b** (412 mg, 0.557 mmol, 53%). **3b**: colorless needles (EtOH-CH_2Cl_2); mp 192.0–193.5°C; ^{1}H NMR (500 MHz, $CDCl_3$, 296 K): δ7.00 (2H, d, $^4J_{PH}$ = 3.2 Hz, Ar-3,5), 6.9763 (2H, dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.7 Hz, pheno-4,6), 6.9758 (2H, dd, $^4J_{HH}$ = 3.0 Hz, $^4J_{PH}$ = 3.3 Hz, Tip-3,5), 6.94 (2H, dd, $^4J_{HH}$ = 3.1 Hz, $^4J_{PH}$ = 2.0 Hz, Tip-3,5), 6.83 (2H, ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.7 Hz, pheno-2,8), 6.78 (2H, td, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, pheno-3,7), 6.25 (2H, dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz, pheno-1,9), 3.56 [4H, septet of doublet, $^3J_{HH}$ = 6.1 Hz, $^4J_{PH}$ = 6.1 Hz, C$\underline{H}$(CH_3)$_2$-2, 6], 2.87 [2H, septet, $^3J_{HH}$ = 6.9 Hz, C$\underline{H}$(CH_3)$_2$-4], 2.25 (6H, d, $^4J_{PH}$ = 5.0 Hz, CH_3), 1.24 [12H, d, $^3J_{HH}$ = 6.9 Hz, CH(C$\underline{H}_3$)$_2$-4], 1.21 [6H, d, $^3J_{HH}$ = 6.7 Hz, CH(C$\underline{H}_3$)$_2$-2,6], 1.19 [6H, d, $^3J_{HH}$ = 6.7 Hz, CH(C$\underline{H}_3$)$_2$-2,6], 0.81 [6H, d, $^3J_{HH}$ = 6.6 Hz, CH(C$\underline{H}_3$)$_2$-2,6], 0.66 [6H, d, $^3J_{HH}$ = 6.7 Hz, CH(C$\underline{H}_3$)$_2$-2,6]; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 296 K): δ 153.33 (d, J_{PC} = 17.7 Hz, Tip-2,6), 153.06 (d, J_{PC} = 17.7 Hz, Tip-2,6), 149.71 (s, Tip-4), 145.07 (d, J_{PC} = 19.4 Hz, Ar-2,6), 144.21 (s, pheno-9a,10a), 139.52 (s, Ar-4), 138.62 (d, J_{PC} = 26.3 Hz, Ar-1), 130.61 (d, J_{PC} = 2.9 Hz, Ar-3,5), 130.37 (d, J_{PC} = 19.4 Hz, Tip-1), 126.66 (s, pheno-2,8 or 4,6), 126.53 (s, pheno-2,8 or 4,6), 122.31 (d, J_{PC} = 4.6 Hz, Tip-3,5), 122.16 (s, pheno-3,7), 122.15 (d, J_{PC} = 4.6 Hz, Tip-3,5), 119.62 (s, pheno-4a,5a),

115.70 (s, pheno-1,9), 34.05 [s, C$\underline{H}$(CH_3)$_2$-4], 32.11 [d, J_{PC} = 11.4 Hz, C$\underline{H}$(CH_3)$_2$-2,6], 31.95 [d, J_{PC} = 12.6 Hz, C$\underline{H}$(CH_3)$_2$-2,6], 24.43 [s, CH(C$\underline{H}_3$)$_2$-2,6], 24.36 [s, CH(C$\underline{H}_3$)$_2$-2,6], 23.88 [s, CH(C$\underline{H}_3$)$_2$-4], 23.56 (d, J_{PC} = 16.0 Hz, C$\underline{H}_3$), 23.55 [s, CH(C$\underline{H}_3$)$_2$-2,6], 23.04 [s, CH(C$\underline{H}_3$)$_2$-2,6]; ^{31}P NMR (81 MHz, $CDCl_3$, 296 K): δ −46.2 (s); FABMS *m/z* (rel intensity) 739 (M^+; 27), 303 (M^+–Tip_2P + 1; 34), 84 (M^+–655; 100).

(2,6-Diisopropyl-4-phenothiazinylphenyl)bis(2,4,6-triisopropylphenyl)phosphine (**3c**): To a solution of **5b** (500 mg, 1.15 mmol) in tetrahydrofuran (20 mL), *t*-butyllithium (1.51 mol L^{-1} in pentane, 1.70 mL, 2.57 mmol) was added at −78°C. The solution was stirred for 60 min and then copper(I) chloride (250 mg, 2.50 mmol) was added. The resultant mixture was warmed to room temperature, stirred for 2 h, and cooled to −78°C. A solution of chlorobis(2,4,6-triisopropylphenyl)phosphine (270 mg, 1.14 mmol) in tetrahydrofuran (5 mL) was added and the resultant mixture was warmed to room temperature, refluxed for 20 h, and concentrated under reduced pressure. The residue was purified by column chromatography (Al_2O_3/*n*-hexane, *n*-hexane/chloroform = 5/1) and GPC (Jaigel 1H + 3H/chloroform) to give **3c** (280 mg, 0.35 mmol, 31%). **3c**: pale yellow solid; mp 81.0–82.0°C; ^{1}H NMR (600 MHz, $CDCl_3$, 296 K): δ 7.06 (2H, d, $^4J_{PH}$ = 2.8 Hz, Ar-3,5), 6.99 (2H, dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.6 Hz, pheno-4,6), 6.95 (4H, d, $^4J_{PH}$ = 3.3 Hz, Tip-3,5), 6.83–6.75 (4H, m, pheno-2,3,7,8), 6.13 (2H, dd, $^4J_{HH}$= 7.8 Hz, $^3J_{HH}$ = 1.3 Hz, pheno-1,9), 3.66–3.58 [2H, m, Ar-C$\underline{H}$(CH_3)$_2$-2,6], 3.57–3.45 [4H, m, Tip-C$\underline{H}$(CH_3)$_2$-2,6], 2.85 [2H, sept, $^4J_{HH}$ = 6.9 Hz, Tip-C$\underline{H}$(CH_3)$_2$-4], 1.22 [12H, d, $^3J_{HH}$ = 6.9 Hz, Tip-CH(C$\underline{H}_3$)$_2$-4], 1.20 [6H, d, $^3J_{HH}$ = 6.8 Hz, Ar-CH(C$\underline{H}_3$)$_2$-2,6], 1.18 [6H, d, $^3J_{HH}$ = 6.8 Hz, Tip-CH(C$\underline{H}_3$)$_2$-2,6], 1.16 [6H, d, $^3J_{HH}$ = 6.7 Hz, Tip-CH(C$\underline{H}_3$)$_2$-2,6], 0.82 [6H, d, $^3J_{HH}$ = 6.7 Hz, Ar-CH(C$\underline{H}_3$)$_2$-2,6], 0.74 [6H, d, $^3J_{HH}$ = 6.6 Hz, Tip-CH(C$\underline{H}_3$)$_2$-2,6], 0.67 [6H, d, $^3J_{HH}$ = 6.5 Hz, TipCH(C$\underline{H}_3$)$_2$-2,6]; ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 296 K): δ 156.49 (d, J_{PC} = 19.0 Hz, Ar-2,6), 153.24 (d, J_{PC} = 18.3 Hz, Tip-2,6), 152.75 (d, J_{PC} = 18.0 Hz, Tip-2,6), 149.69 (s, Tip-4), 144.42 (s, pheno-9a,10a), 141.04 (s, Ar-4), 136.76 (d, J_{PC} = 27.2 Hz, Ar-1), 131.01 (d, J_{PC} = 23.1 Hz, Tip-1), 126.79 (s, pheno-2,8), 126.54 (s, pheno-4,6), 126.36 (d, J_{PC} = 3.5 Hz, Ar-3,5), 122.20 (d, J_{PC} = 4.2 Hz, Tip-3,5), 122.17 (d, J_{PC} = 3.9 Hz, Tip-3,5), 122.11 (s, pheno-3,7), 119.24 (s, pheno-4a,5a), 115.32 (s, pheno-1,9), 34.10 [s, Tip-C$\underline{H}$(CH_3)$_2$-4], 32.34 [d, J_{PC} = 16.7 Hz, Tip-C$\underline{H}$(CH_3)$_2$-2,6], 32.11 [d, J_{PC} = 17.7 Hz, Tip-C$\underline{H}$(CH_3)$_2$-2,6], 31.93 [d, J_{PC} = 18.6 Hz, Ar-C$\underline{H}$(CH_3)$_2$-2,6], 24.58 [s, Ar-CH(C$\underline{H}_3$)$_2$-2,6], 24.53 [s, Tip-CH(C$\underline{H}_3$)$_2$-2,6], 24.44 [s, Tip-CH(C$\underline{H}_3$)$_2$-2,6], 23.92 [s, Tip-CH(C$\underline{H}_3$)$_2$-4,4], 23.90 [s, Tip-CH(C$\underline{H}_3$)$_2$-4,4], 23.19 [s, Ar-CH(C$\underline{H}_3$)$_2$-2,6], 23.16 [s, Tip-CH(C$\underline{H}_3$)$_2$-2,6], 22.51 [s, Tip-CH(C$\underline{H}_3$)$_2$-2,6]; ^{31}P NMR (162 MHz, $CDCl_3$, 296 K): δ −50.1 (s); LRMS (70 eV, EI) *m/z* (rel intensity) 795 (M^+; 100), 438 (M^+−Ar; 6), 359 (M^+−Tip_2P; 3), 198 (Tip; 15).

Chlorobis(2,6-diisopropyl-4-phenothiazinylphenyl)phosphine (**6**): To a solution of **5b** (1.26 g, 2.88 mmol) in tetrahydrofuran (40 mL), butyllithium (1.57 mol L^{-1} in *n*-hexane, 2.20 mL, 3.45 mmol) was added at −78°C. The solution was stirred for 60 min and then phosphorus trichloride (0.15 mL, 1.72 mmol) was added. The resultant mixture was warmed to room temperature, stirred for 12 h, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2,*n*-hexane/chloroform = 5/1) to give crude **6** (290 mg, 0.370 mmol, 26%). **6**: colorless solid; ^{1}H NMR (400 MHz, C_6D_6, 296 K):δ 7.24 (4H, d, $^4J_{PH}$ = 2.8 Hz, Ar-3,5), 7.10 (4H, dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, pheno-4,6), 6.83 (4H, td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, pheno-2,8), 6.73 (4H, td, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.1 Hz, pheno-3,7), 6.50 (4H, dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz, pheno-1,9), 4.15–4.05 [4H, m, C$\underline{H}$(CH_3)$_2$], 1.11 [12H, d, $^3J_{HH}$ = 6.7 Hz, CH(C$\underline{H}_3$)$_2$], 1.07 [12H, d, $^3J_{HH}$ = 6.7 Hz, CH(C$\underline{H}_3$)$_2$]; ^{31}P NMR (162 MHz, $CDCl_3$, 296 K): δ 85.0 (s).

Attempted Synthesis of Tris(2,6-diisopropyl-4-phenothiazinylphenyl)phosphine: To a solution of **5b** (210 mg, 0.48 mmol) in tetrahydrofuran (10 mL), *t*-butyllithium (1.60 mol L^{-1} in pentane, 0.70 mL, 1.12 mmol) was added at −78°C. The solution was stirred for 60 min and then copper(I) chloride (110 mg, 1.10 mmol) was added. The resultant mixture was warmed to room temperature, stirred for 12 h, and cooled to −78°C. A solution of **6** (290 mg, 0.37 mmol) in tetrahydrofuran (5 mL) was added and the resultant mixture was warmed to room temperature, refluxed for 12 h, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, *n*-hexane/chloroform = 5/1) and GPC (Jaigel 1H + 3H/chloroform) to give **4** (140 mg, 0.09 mmol, 8%). **4**: pale yellow solid; mp 61.0–61.5°C (decomp); ^{1}H NMR (400 MHz, C_6D_6, 296 K): δ 7.20 (2H, brs, Ar-3,5), 7.15 (4H, brs, Ar-3,5), 7.15–7.08 (2H + 8H, m, Ar-3,5, pheno-4,6), 6.95–6.86 (8H, m, pheno-2,8), 6.80–6.71 (8H, m, pheno-3,7), 6.46 (4H, d, $^3J_{HH}$ = 8.4 Hz, pheno-1,9), 5.35–5.18 [2H, m, C$\underline{H}$(CH_3)$_2$-2,6], 4.20–4.10 [2H + 2H, m, C$\underline{H}$(CH_3)$_2$-2,6], 3.90 [2H, sept, $^3J_{HH}$ = 6.4 Hz, C$\underline{H}$(CH_3)$_2$-2,6], 1.29 [6H, d, $^3J_{HH}$= 6.0 Hz, CH(C$\underline{H}_3$)$_2$-2,6], 1.25 [6H + 6H, d, $^3J_{HH}$ = 7.2 Hz, CH(C$\underline{H}_3$)$_2$-2,6],

1.23 [6H, d, $^3J_{HH}$ = 7.2 Hz, CH(C$\underline{H}_3$)$_2$-2,6], 0.81 [6H, d, $^3J_{HH}$ = 6.4 Hz, CH(C$\underline{H}_3$)$_2$-2,6], 0.75 [6H, d, $^3J_{HH}$ = 6.8 Hz, CH(C$\underline{H}_3$)$_2$-2,6], 0.48 [6H, d, $^3J_{HH}$ = 6.8 Hz, CH(C$\underline{H}_3$)$_2$-2,6], 0.47 [6H, d, $^3J_{HH}$ = 7.2 Hz, CH(C$\underline{H}_3$)$_2$-2,6]; ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 296 K): δ 158.93 (pseudo t, $J_{PC} + J_{P'C}$ = 39.6 Hz, Ar-2,6), 158.39 (pseudo t, $J_{PC} + J_{P'C}$ = 8.9 Hz, Ar-2,6), 158.08 (pseudo t, $J_{PC} + J_{P'C}$ = 35.2 Hz, Ar-2,6), 157.91 (s, Ar-2,6), 144.81 (s, pheno-9a,10a), 144.77 (s, pheno-9a,10a), 143.70 (s, Ar-4), 142.56 (s, Ar-4), 133.74 (pseudo t, $J_{PC} + J_{P'C}$ = 38.1 Hz, Ar-1), 133.43 (pseudo t, $J_{PC} + J_{P'C}$ = 30.1 Hz, Ar-1), 129.67, 128.64, 127.90, 127.46, 127.38, 126.84 (s × 8, several peaks were accidentally overlapped with the signals of the solvent, Ar-3,5, pheno-2,8,4,6), 123.14 (s, pheno-3,7), 123.04 (s, pheno-3,7), 121.22 (s, pheno-4a,5a), 120.61 (s, pheno-4a,5a), 116.34 (s, pheno-1,9), 115.94 (s, pheno-1,9), 33.00 (s, C$\underline{H}$(CH$_3$)$_2$-2,6), 32.60 [pseudo t, $J_{PC} + J_{P'C}$ = 38.9 Hz,, C$\underline{H}$(CH$_3$)$_2$-2,6], 32.44 [pseudo t, $J_{PC} + J_{P'C}$ = 41.1 Hz, C$\underline{H}$(CH$_3$)$_2$-2,6], 31.99 [pseudo t, $J_{PC} + J_{P'C}$ = 35.2 Hz, C$\underline{H}$(CH$_3$)$_2$-2,6], 25.55 [s, CH(C$\underline{H}_3$)$_2$-2,6], 24.93 [s, CH(C$\underline{H}_3$)$_2$-2,6], 24.14 [s, CH(C$\underline{H}_3$)$_2$-2,6], 24.06 [s, CH(C$\underline{H}_3$)$_2$-2,6], 23.67 [s, CH(C$\underline{H}_3$)$_2$-2,6], 23.61 [s, CH(C$\underline{H}_3$)$_2$-2,6], 23.45 [s, CH(C$\underline{H}_3$)$_2$-2,6], 22.52 [s, CH(C$\underline{H}_3$)$_2$-2,6]; ^{31}P NMR (162 MHz, C_6D_6, 296 K): δ −35.9 (s); LRMS (70 eV, EI) *m/z* (rel intensity) 1494 (M^+; 2), 1136 (M^+−Ar; 1), 748 (M^+−Ar_2P; 100), 388 (M^+−Ar; 16).

*Tetrakis(2,6-diisopropyl-4-phenothiazinylphenyl) diphosphane (**4**)*: To a solution of **5b** (500 mg, 1.16 mmol) in tetrahydrofuran (20 mL), *t*-butyllithium (1.60 mol L^{-1} in pentane, 1.55 mL, 2.49 mmol) was added at −78°C. The solution was stirred for 60 min and then phosphorus trichloride (0.05 mL, 0.57 mmol) was added. The resultant mixture was warmed to room temperature, stirred for 12 h, and concentrated under reduced pressure to give **6**. To a mixture of magnesium (50.0 mg, 2.08 mmol) in tetrahydrofuran (10 mL), a solution of **6** in tetrahydrofuran (10 mL) was added at 0°C. The resultant mixture was warmed to room temperature, stirred for 12 h, refluxed for 12 h, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2/*n*-hexane, *n*-hexane/chloroform = 5/1) to give **4** (80 mg, 0.06 mmol, 19%).

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