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Synthesis of crowded triarylphosphines carrying functional sites

Shigeru Sasaki *, Fumiki Murakami, Midori Murakami, Mariko Watanabe, Kiyotoshi Kato, Katsuhide Sutoh, Masaaki Yoshifuji *

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan

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Abstract

4,4′-Diphosphinobiaryls and 1,3- and 1,4-borylphosphinobenzenes carrying crowded triarylphosphine moieties were synthesized by reaction of the corresponding diarylchlorophosphine with an arylcopper(I) reagent. Intramolecular interaction of the phosphorus redox center with the other phosphorus or the boron redox center was investigated by cyclic voltammetry. 4,4′-Diphosphinobiaryls displayed two-step reversible redox waves with slight differences of the oxidation potentials due to weak interaction between two phosphorus redox centers across 4,4′-biarylene linkage. Borylphosphinobenzenes showed two step redox waves corresponding to oxidation at the phosphorus and reduction at the boron. Although significant interaction between the phosphorus and boron redox centers was not observed in the cyclic voltammograms due to large difference of the redox potentials between phosphorus and boron redox centers, an absorption due to weakly interacting phosphorus and boron was observed in the UV–Vis spectrum of the 1,4-borylphosphinobenzene.

Keywords: Triarylphosphine; Biaryl; Triarylborane; Cyclic voltammetry

1. Introduction

Crowded triarylphosphines such as trimesitylphosphine (**1**) [1] have a unique structure represented by large bond angles and lengths around phosphorus and some of them are reversibly oxidized to persistent cation radicals at low oxidation potentials since structural deformation around the phosphorus raises the HOMO and bulky aryl groups kinetically stabilize the cation radicals (Scheme 1) [2]. We recently synthesized one of the most crowded triarylphosphines known so far, tris(2,4,6-triisopropylphenyl)phosphine (**2**), and determined its structure and revealed redox properties [3]. We are also interested in construction of the multistep redox systems composed of phosphorus redox centers and synthesized compounds carrying both phosphorus and the other redox sites since such investigations are expected to lead to better understanding of newly developed structures as well as to construction of practical functional molecules [4]. Since crowded triarylphosphines are expected to be good candidates for the redox site, we first attempted synthesis of aminophosphinobenzenes carrying a crowded triarylphosphine moiety similar to **1**, and considerable donor–donor, phosphorus–nitrogen, interaction was observed although the cyclic voltammograms were irreversible due to instability of the corresponding dication diradical [5]. Herein we report the synthesis and redox properties of 4,4′-diphosphinobiaryls **3a**, **3b** and borylphosphinobenzenes **4a**, **4b**. 4,4′-Diphosphinobiaryls **3a** and **3b** were synthesized to study intramolecular interaction of two crowded triarylphosphine moieties. On the other hand, the crowded triarylborane moieties were chosen to investigate donor–acceptor interaction

* Corresponding authors. Tel.: +81 22 217 6558; fax: +81 22 217 6562.
E-mail addresses: yoshifj@mail.tains.tohoku.ac.jp (M. Yoshifuji), sasaki@mail.tains.tohoku.ac.jp (S. Sasaki).

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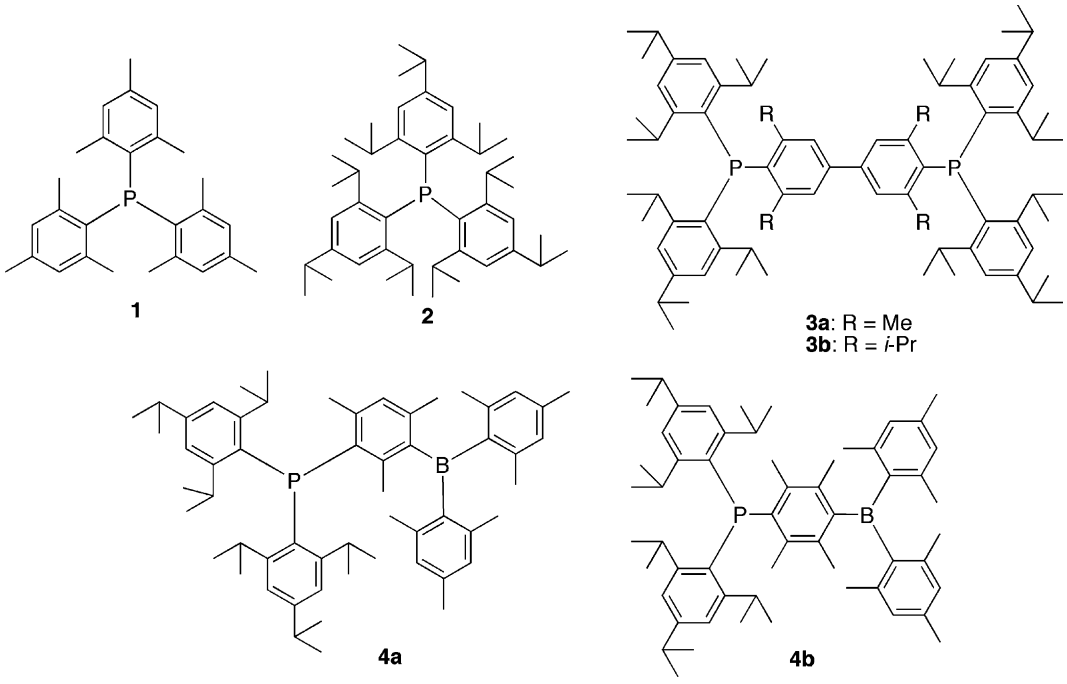


Scheme 1. Crowded triarylphosphines.

with the crowded triarylphosphine, since trimesitylborane was reported to be a weak acceptor and to give the corresponding anion radical as a stable molecule [6].

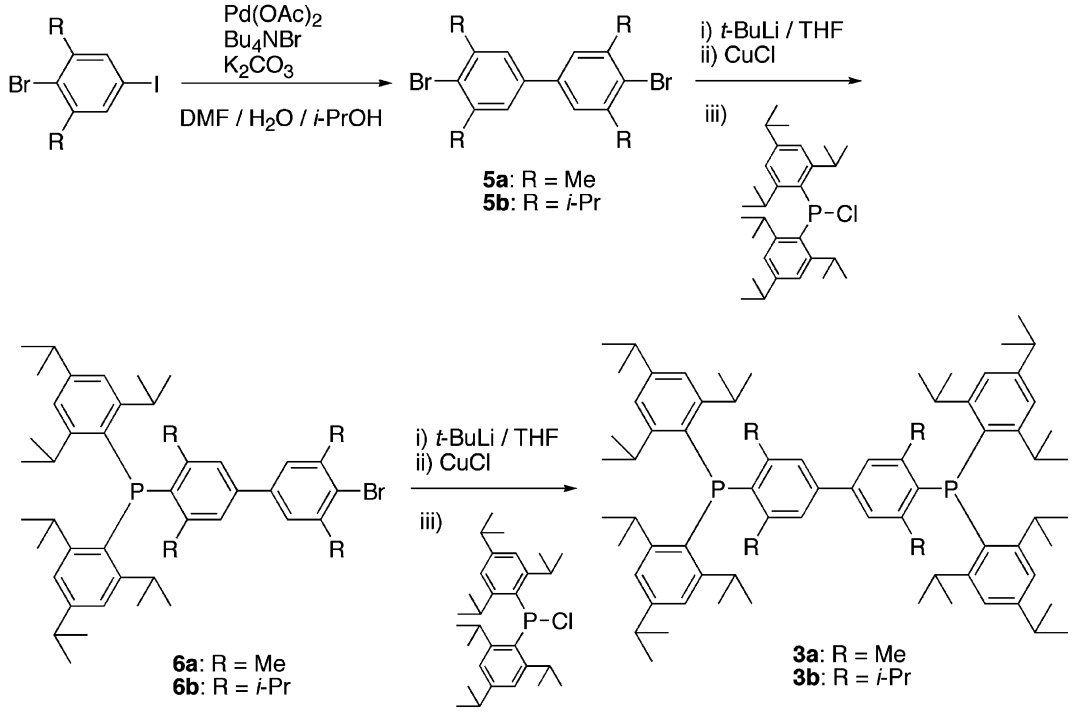
2. Results and discussion

2.1. Synthesis and characterization

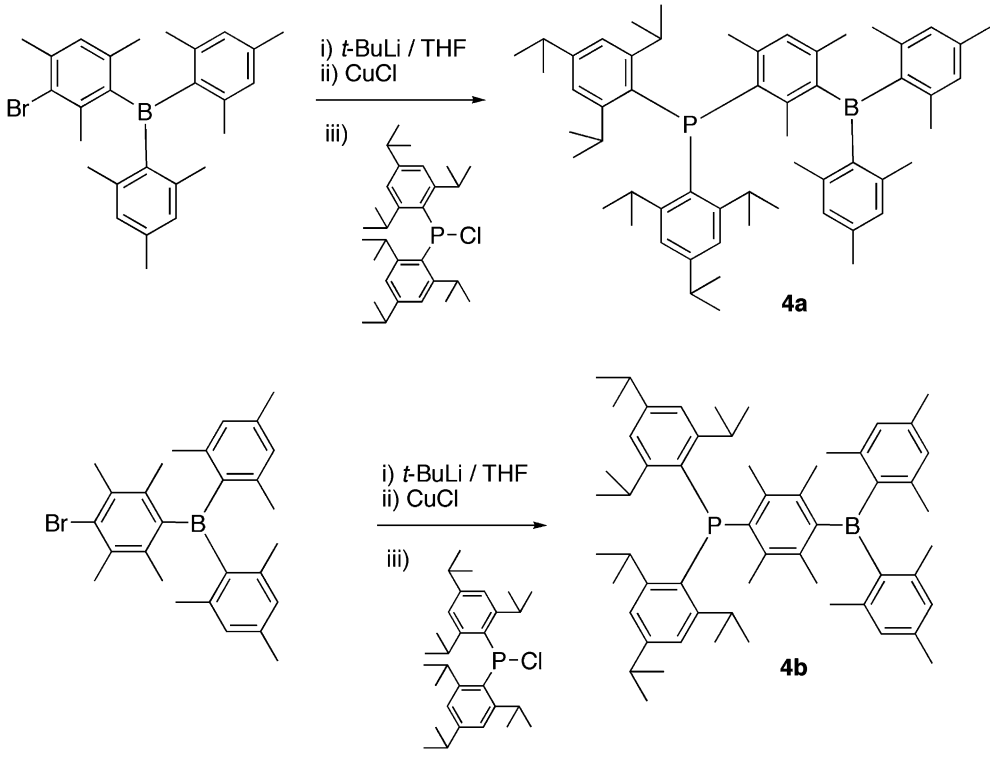
4,4′-Dibromobiaryls **5a** [7], **5b** were synthesized by Pd-catalyzed coupling of the corresponding bromoiodobenzenes [8] (Scheme 2). Two bis(2,4,6-triisopropylphenyl)phosphino groups were successively introduced by the reaction of the corresponding arylcopper(I) reagent, which was prepared in situ by lithiation of **5a**, **5b** or **6a**, **6b** followed by addition of CuCl, with chlorobis(2,4,6-triisopropylphenyl)phosphine [9] and diphosphine **3a** and **3b** were isolated as colorless solids. Borylphosphinobenzenes **4a**, **4b** were also synthesized by the reaction of the arylcopper(I) reagent, which were prepared from borylbromobenzenes [10], with chlorobis(2,4,6-triisopropylphenyl)phosphine and isolated as yellow solids (Scheme 3). ^{31}P NMR spectra of 4,4′-diphosphinobiaryls **3a** (δ_P −45.9, −46.2), **3b** (δ_P −50.07, −51.12) and borylphosphinobenzenes **4a** (δ_P −46.6, −47.3), **4b** (δ_P −42.1, −42.5) consisted of two closely-spaced singlet peaks in the high field region typical of crowded triarylphosphines. Since diphosphines **3a**, **3b** as well as borylphosphinobenzenes **4a**, **4b** have two crowded propellers consisting of three aromatic rings, there can be diastereomers arising from the helicity of the propellers and they can be separately observed if the enantiomerization of the propellers is slow as compared with the time scale of ^{31}P NMR. ^{1}H NMR spectra of **6a**, **6b** as well as **3a**, **3b**, **4a**, **4b** around 293 K also supported this interpretation since two 2,4,6-triisopropylphenyl groups attached to the same phosphorus atom were observed as if they were inequivalent aromatic groups and *C*2-symmetrical relative to *P–C* axis. On the other hand, only one 2,4,6-triisopropylphenyl group which was *C*2-symmetrical relative to *P–C* axis was observed for phosphine **2** [3].

2.2. Redox properties

Cyclic voltammograms of **3a** and **3b** consisted of two-step reversible waves with slight differences of the oxidation potentials (Fig. 1, Table 1). 4,4′-Diphosphinobiaryl **3b**, which has more crowded triarylphosphine moieties, was oxidized at lower potential than **3a**. Two phosphorus atoms separated by biarylene bridge still have communication with each other and **3a** and **3b** can be oxidized in a stepwise manner. Chemical oxidation of **3a** and **3b** with tris(4-bromophenyl)aminium perchlorate and silver perchlorate in dichloromethane, respectively, afforded brown solutions, which were different from the pink to purple color typical of cation radicals such as $\mathbf{1}^{+\cdot}$ or $\mathbf{2}^{+\cdot}$ (Fig. 2). However, EPR spectra of the solution (**3a**: $g = 2.007$, $a(P) = 23.7$ mT, **3b**: $g = 2.007$, $a(P) = 23.7$ mT) as well as the frozen solution (**3a**: $g_\perp = 2.010$, $a_\perp(P) = 12.0$ mT, $g_\parallel = 2.003$, $a_\parallel(P) = 39.9$ mT, **3b**: $g_\perp = 2.009$, $a_\perp(P) = 11.3$ mT, $g_\parallel = 2.002$, $a_\parallel(P) = 41.5$ mT) were nearly identical with those of cation radicals such as $\mathbf{2}^{+\cdot}$ [3] and a $\Delta m_s = 2$ transition



Scheme 2. Synthesis of 4,4′-diphosphinobiphenyls.



Scheme 3. Synthesis of borylphosphinobenzenes.

typical of a triplet state was lacking. Since phosphorus centered cation radicals such as $\mathbf{2}^{+\cdot}$ have considerable unpaired electron density on the phosphorus atom, intramolecular exchange as well as dipole–dipole interaction across 4,4′-biarylene bridge could be very weak and we could not conclude from the EPR spectra if we observed a dication diradical or a cation radical generated by decomposition of $\mathbf{3}^{2(+\cdot)}$.

Cyclic voltammograms of **4a** and **4b** consisted of a reversible redox wave and a quasi-reversible redox wave

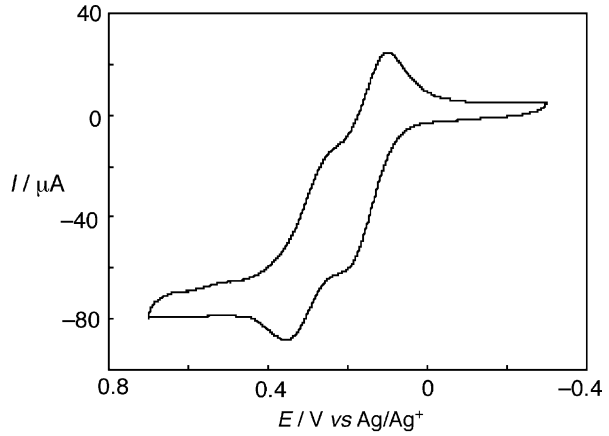


Fig. 1. Cyclic voltammograms of 4,4′-diphosphinobiphenyls **3b** in dichloromethane.

Table 1
Redox potentials of **3a** and **3b**

Compounds	$^1E_{1/2}$/V	$^2E_{1/2}$/V	ΔE/V
3a	0.24	0.36	0.12
3b	0.19	0.35	0.16

Measured at 295 K in dichloromethane with 0.1 M n-Bu_4NClO_4 as a support electrolyte. Working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/0.01 M $AgNO_3$ in acetonitrile with 0.1 M n-Bu_4NClO_4.
($^1E_{1/2}$Ferrocene/Ferricinium) = 0.18 V). Scan rate = 30 mV s^{-1}.

with significant differences of the oxidation potentials (Fig. 3, Table 2). Since crowded triarylboranes such as trimesitylborane are weak electron acceptors with high reduction potential though some of the corresponding anion radical allowed isolation, clear evidence of interaction between the phosphorus and boron redox centers was not observed by cyclic voltammetry. Although there was no significant difference between cyclic voltammograms of the 1,3-derivative **4a** and the 1,4-derivative **4b**, marked difference was observed between UV–Vis spectra of **4a** and **4b** (Fig. 4). 1,4-Borylphosphinobenzene **4b** exhibited an absorption at λ_{max} = 385 nm as well as at 324 nm; on the other hand, **4a** showed a single absorption maximum at 330 nm, which was close to λ_{max} of the crowded triarylphosphines and boranes (**1**: 314 nm, **2**: 327 nm, Mes_3B: 330 nm) [1,3,6]. Since only 1,4-derivative **4b** showed absorption at longer wavelength, a quinoid-type structure in the excited state (Scheme 4), which was postulated to explain a similar red shift observed in 1,4-aminoborylbenzenes [8], was considered to contribute significantly. A downfield shift of the ^{31}P resonance of **4b** was also consistent with this observation.

3. Conclusion

4,4′-Diphosphinobiaryls **3a**, **3b** and borylphosphinobenzenes **4a**, **4b** carrying crowded triarylphosphine moieties were synthesized by the reaction of arylcopper(I) reagents with chlorophosphines. Two triarylphosphine moieties of **3a** and **3b** were reversibly oxidized in two steps with the slight difference of oxidation potentials. However, dipole–dipole and exchange interaction typical of diradicals were probably too small to be detected in EPR, although diphosphine **3b**, which has two triarylphosphine moieties as crowded as **2**, was expected to give a stable dication-diradical system. Investigation on the diphosphines carrying crowded triarylphosphine moieties separated by various linkages will provide further insight into phosphorus–phosphorus interaction. Phosphorus–boron intramolecular interaction observed in cyclic voltammograms of **4a** and **4b** was weak since the triarylborane moieties employed were too weak as acceptors, however, UV–Vis spectrum of **4b** suggested considerable intramolecular interaction such as charge transfer in crowded triarylphosphines connected to stronger acceptors.

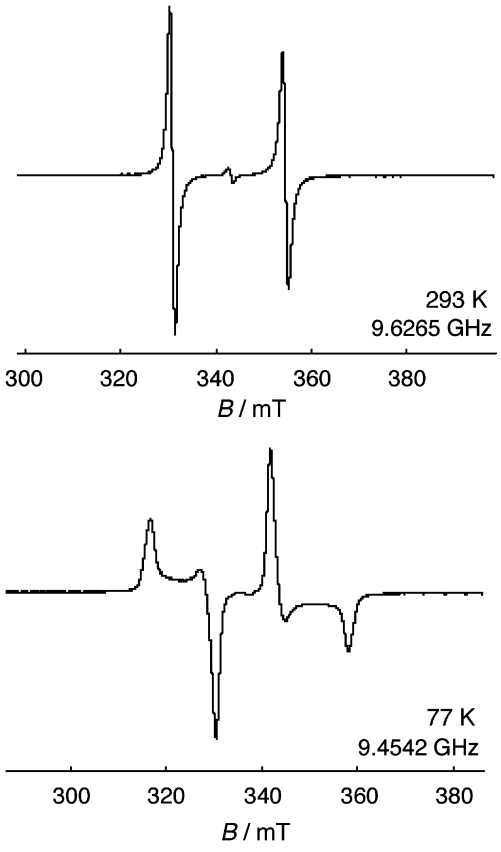


Fig. 2. EPR spectra obtained after oxidation of **3b** with silver perchlorate in dichloromethane.

4. Experimental

4.1. General

The ^1H, ^{13}C, and ^{31}P NMR spectra were measured on Bruker AC200P, AV400, or JEOL α-500 spectrometers.

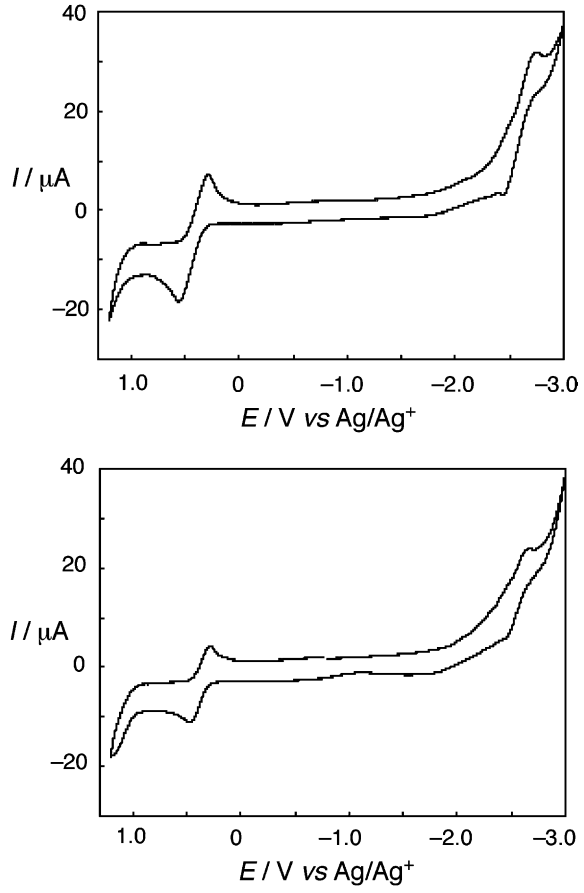


Fig. 3. Cyclic voltammograms of borylphosphinobenzenes **4a** (top) and **4b** (bottom) in tetrahydrofuran.

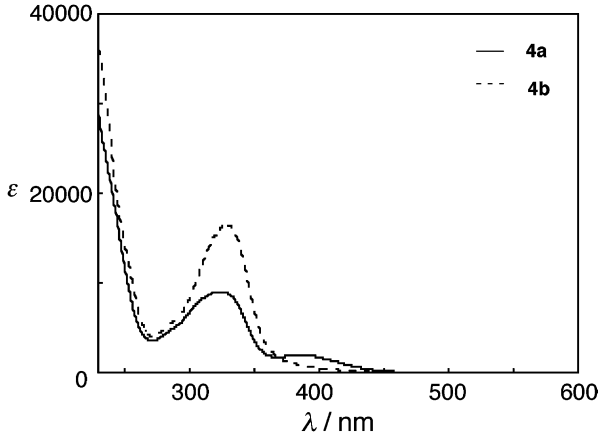
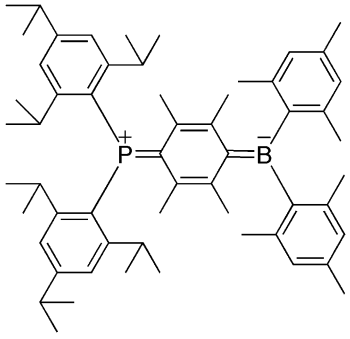


Fig. 4. UV–Vis spectra of borylphosphinobenzenes **4a** and **4b** in dichloromethane.



Scheme 4.

Table 2
Redox potentials of **4a** and **4b**

Compounds	$^{ox}E_{1/2}$/V	$^{Red}E_{1/2}$/V	ΔE/V
4a	0.42	−2.58	3.00
4b	0.38	−2.55	2.93

Measured at 293 K in tetrahydrofuran with 0.1 M n-Bu_4NClO_4 as a support electrolyte. Working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/0.01 M $AgNO_3$ in acetonitrile with 0.1 M n-Bu_4NClO_4.
($^1E_{1/2}$Ferrocene/Ferricinium) = 0.17 V). Scan rate = 30 mV s^{-1}.

The ^1H and ^{13}C NMR chemical shifts are expressed as δ downfield from external tetramethylsilane. The chemical shifts were calibrated to the residual proton of the deuterated solvent (δ 7.25 for chloroform-*d*) or the carbon of the deuterated solvent (δ 77.0 for chloroform-*d*). The ^{31}P NMR chemical shifts are expressed as δ downfield from external 85% H_3PO_4. The mass spectra were measured on a Hitachi M-2500S with electron impact (EI) ionization at 70 eV or a JEOL HX-110 with fast atom bombardment (FAB) ionization using the *m*-nitrobenzyl alcohol matrix. FT-ICR-MS spectra were measured on a Bruker APEX3 with electron spray ionization (ESI). Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. UV–Vis spectra were measured on a Hitachi U-3210 spectrometer. Microanalyses were performed at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. Merck silica gel 60 and Sumitomo basic alumina (KCG-30) were used for column chromatography. Gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 recycling preparative HPLC equipped with JAIGEL 1H + 2H columns. All reactions were carried out under argon. Tetrahydrofuran was distilled from sodium benzophenone ketyl under argon just prior to use. Cyclic voltammetry was performed with a BAS CV-50W controller with glassy carbon, Pt wire, and Ag/0.01 M $AgNO_3$/0.1 M n-Bu_4NClO_4/CH_3CN as a working, counter, and reference electrodes, respectively. A substrate ca. 10^{-4} M was dissolved in dichloromethane or tetrahydrofuran with 0.1 M 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 at a room temperature and 77 K. A JEOL ES-UCD2X liquid nitrogen Dewar was used for measurement at 77 K.

Samples were dissolved in dichloromethane, which was distilled over calcium hydride, degassed by freeze-and-thaw cycles and transferred to a sample by bulb-to-bulb distillation. Oxidation was carried out in an H-shaped sealed tube and tris(4-bromophenyl)aminium perchlorate and silver perchlorate were used as oxidant for **3a** and **3b**, respectively.

4.2. Synthesis

4.2.1. Chlorobis(2,4,6-triisopropylphenyl)phosphine

To a solution of 2-bromo-1,3,5-triisopropylbenzene (17.7 g, 62.5 mmol) in tetrahydrofuran (100 mL) was added *n*-butyllithium (41.0 mL, 1.56 M in *n*-hexane, 64.0 mmol) at −78 °C in 5 min. After being stirred for 30 min at −78 °C, phosphorus trichloride (2.7 mL, 30.9 mmol) was added to the reaction mixture at −78 °C. The mixture was stirred for 30 min at −78 °C and gradually warmed to room temperature and stirred for 2 h. After removal of the solvent, the residue was submitted to column chromatography (SiO_2, *n*-hexane) to give 13.4 g (28.4 mmol, 92%) of chlorobis(2,4,6-triisopropylphenyl)phosphine.

Chlorobis(2,4,6-triisopropylphenyl)phosphine: colorless prisms; m.p. 52.0–54.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 6.94 (4H, d, $^4J_{PH}$ = 2.40 Hz, arom.-3,5), 3.72 (4H, brm, C*H*$(CH_3)_2$-2,6), 2.82 (2H, septet, $^3J_{HH}$ = 6.80 Hz, C*H*$(CH_3)_2$-4), 1.19 (12H, d, $^3J_{HH}$ = 6.81 Hz, CH(C*H*$_3)_2$-4), 1.01 (12H, d, $^3J_{HH}$ = 6.79 Hz, CH(C*H*$_3)_2$-2,6), 0.98 (6H, d, $^3J_{HH}$ = 6.81 Hz, CH(C*H*$_3)_2$-2,6); ^{13}C NMR (101 MHz, $CDCl_3$, 296 K) δ151.48 (d, J_{PC} = 16.0 Hz, arom.-2,6), 150.24 (s, arom.-4), 134.17 (d, J_{PC} = 50.6 Hz, arom.-1), 122.44 (d, J_{PC} = 1.8 Hz, arom.-3,5), 34.12 (s, *C*H$(CH_3)_2$-4), 31.30 (d, J_{PC} = 18.4 Hz, *C*H$(CH_3)_2$-2,6), 24.56 (s, CH(*C*H$_3)_2$-4), 23.84 (s, CH(*C*H$_3)_2$-2,6), 23.80 (s, CH(*C*H$_3)_2$-2,6), 23.68 (s, CH(*C*H$_3)_2$-2,6); ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) δ 89.9(s); LRMS (70 eV, EI) *m*/*z* (rel. intensity) 474 (M^+ + 2; 12), 472 (M^+; 33), 438 (Tip_2P^+ + 1; 38), 429 (M^+ − *i*-Pr; 100), 268 (TipPCl$^+$ + 1; 14).

4.2.2. Bromo-5-iodo-1,3-diisopropylbenzene

To a mixture of 2,6-diisopropyl-4-iodoaniline (8.27 g, 27.3 mmol) in acetic acid (65 mL) and conc. sulfuric acid (30 mL) was added isopentyl nitrite (6.8 mL, 50.6 mmol) in 10 min at 0 °C and the mixture was stirred for 25 min at 0 °C. To a solution of copper(I) bromide (5.52 g, 38.5 mmol) in hydrobromic acid (47–49%, 100 mL) was added the mixture of the diazonium salt in 30 min at 0 °C and the mixture was gradually warmed to 20 °C, stirred for 14 h, and further stirred at 80 °C for 15 min. The reaction mixture was poured onto ice-water, extracted with *n*-hexane, washed with $NaHSO_3$ solution and saturated NaCl solution, and dried over anhydrous magnesium sulfate. The mixture was filtered, concentrated in vacuo, and purified by column chromatography (SiO_2, *n*-hexane) to afford 2-bromo-5-iodo-1,3-diisopropylbenzene (7.76 g, 21.1 mmol, 77%).

2-Bromo-5-iodo-1,3-diisopropylbenzene: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 7.38 (s, 2H, arom.), 3.41 (sept, 2H, J_{HH} = 6.83 Hz, C*H*$(CH_3)_2$-1,3), 1.22 (d, 12H, J_{HH} = 6.62 Hz, CH(C*H*$_3)_2$-1,3); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K) δ 150.52 (s, arom-1,3), 133.82 (s, arom-2), 127.04 (s, arom-4,6), 94.15 (s, arom-2), 33.92 (s, *C*H$(CH_3)_2$-1,3), 23.36 (s, CH(*C*H$_3)_2$-1,3).; LRMS (EI, 70 eV) *m*/*z* (rel. intensity) 368 (M^+ + 2; 99), 366 (M^+; 100), 353 ($M^+ + 2 - CH_3$; 65), 351 ($M^+ - CH_3$; 67), 226 ($M^+ + 2 - CH_3 - I$; 5), 224 ($M^+ - CH_3 - I$; 6), 211 ($M^+ + 2 - 2\times CH_3 - I$; 5), 209 ($M^+ - 2\times CH_3 - I$; 5); HRMS (EI, 70 eV). Found: *m*/*z* 365.9481. Calc. for $C_{12}H_{16}BrI$: M, 365.9480.

4.2.3. 4,4′-Dibromo-3,3′,5,5′-tetramethylbiphenyl (**5a**)

A mixture of 2-bromo-5-iodo-1,3-dimethylbenzene [11] (2.50 g, 8.05 mmol), tetra-*n*-butylammonium bromide (1.33 g, 4.11 mmol), palladium(II) acetate (91.2 mg, 0.406 mmol), potassium carbonate (1.10 g, 7.99 mmol) in DMF (0.9 mL), water (0.35 mL), and isopropyl alcohol (1.25 mmol) was heated at 115 °C for 12 h. The reaction mixture was extracted with ether, washed with saturated NaCl solution, and dried over anhydrous magnesium sulfate. After removal of the drying agent and the solvent, the residue was submitted to column chromatography (silica gel, *n*-hexane) to give **5a** (1.12 g, 3.05 mmol,76%).

5a: colorless needles; m.p. 150.0–152.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (4H, s, arom.), 2.47 (12H, s, Me); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.65 (s, arom.-1,1′), 138.53 (s, arom.-3,3′,5,5′), 126.77 (s, arom.-4,4′), 126.61 (s, arom.-2,2′,6,6′), 23.97 (s, Me-3,3′5,5′); LRMS (70 eV, EI) *m*/*z* (rel. intensity) 370 (M^+ + 4; 50), 368 (M^+ + 2; 100), 366 (M^+; 51), 289 (M^+ + 2 − Br; 7), 287 (M^+ − Br; 6), 208 (M^+ − 2Br; 4); HRMS (70 eV, EI). Found: *m*/*z* 365.9643. Calc. for $C_{16}H_{16}Br_2$: M, 365.9646.

4.2.4. 4,4′-Dibromo-3,3′,5,5′-tetraisopropylbiphenyl (**5b**)

A mixture of 2-bromo-5-iodo-1,3-diisopropylbenzene (2.97 g, 8.14 mmol), tetra-*n*-butylammonium bromide (1.32 g, 4.09 mmol), potassium carbonate (1.14 g, 8.25 mmol), palladium acetate (0.13 g, 0.41 mmol), water (1.5 mL), isopropyl alcohol (6 mL), and *N*,*N*-dimethylformamide (4 mL) was stirred for 40 h at 120 °C similarly to **5a** to afford **5b** (1.15 g, 2.40 mmol, 59%).

5b: colorless crystals; m.p. 96.0–98.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 7.26 (4H, s, arom.), 3.77 (4H, sept, $^3J_{HH}$ = 6.84 Hz, C*H*$(CH_3)_2$), 1.32 (24H, d, $^3J_{HH}$ = 6.87 Hz, CH(C*H*$_3)_2$); ^{13}C NMR (101 MHz, $CDCl_3$, 296 K) δ 148.57 (s, arom.-3,3′,5,5′), 140.90 (s, arom.-1,1′), 126.35 (s, arom.-4,4′), 123.57 (s, arom-2,2′6,6′), 34.09 (s, *C*H$(CH_3)_2$), 23.52 (s, CH(*C*H$_3)_2$);

Anal. Calc. for $C_{24}H_{32}Br_2$: C, 60.02; H, 6.71; Br, 33.27. Found: C, 59.494; H, 6.503; Br, 32.68%.

4.2.5. Bis(2,4,6-triisopropylphenyl)(4′-bromo-3,3′,5′,5′-tetramethyl-4-biphenylyl)phosphine (*6a*)

To a solution of **5a** in tetrahydrofuran (30 mL) was added *n*-butyllitium (1.8 mL, 1.52 M in *n*-hexane) at −78 °C. After being stirred for 15 min, copper(I) chloride (312 mg, 3.16 mmol) was added to the reaction mixture at −78 °C. The mixture was gradually warmed to room temperature and stirred for 12 h. Chlorobis(2,4,6-triisopropylphenyl)phosphine (1.27 g, 2.69 mmol) was dissolved in tetrahydrofuran (15 mL) and the solution was added to the reaction mixture and refluxed for 24 h. After cooling to room temperature, *n*-hexane was added and the suspension was filtrated by Celite. The mixture was purified by column chromatography (silica gel, *n*-hexane to *n*-hexane/ethyl acetate (50:1, v/v) to give **6a** (1.31 g, 1.80 mmol, 67%).

6a: pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$, 295 K) δ 7.32 (2H, s, arom.-2′,6′), 7.16 (2H, d, $^4J_{PH}$ = 3.2 Hz, arom.-2,6), 6.93 (2H, d, $^4J_{PH}$ = 2.8 Hz, arom.-3″,5″), 6.93 (2H, d, $^4J_{PH}$ = 2.8 Hz, arom.-3″,5″), 3.49 (4H, septet, $^3J_{HH}$ 6.9 Hz, C*H*(CH$_3$)$_2$-2″,6″), 2.84 (2H, septet, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$-4″), 2.47 (6H, s, CH$_3$-3′-5′), 2.26 (3H, s, CH$_3$-3-5), 2.25 (3H, s, CH$_3$-3-5), 1.25 (6H, d, $^3J_{HH}$ = 6.2 Hz, CH(C*H*$_3$)$_2$-2″,6″), 1.22 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$-4″), 1.15 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$-2″,6″), 0.72 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$-2″,6″), 0.56 (6H, d, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)$_2$-2″,6″); ^{31}P NMR (81 MHz, $CDCl_3$) δ = −46.3 (s); FABMS *m*/*z* (rel. intensity) 726 (M^+ + 2; 18), 724 (M^+; 16), 646 (M^+ − Br + 1; 23), 542 (M^+ − 4Me − *i*-Pr − Br; 100), 499 (M^+ − 4Me − 2*i*-Pr − Br; 24); HRMS (70 eV, EI). Found: *m*/*z* 724.3799. Calc. for $C_{46}H_{62}PBr$: M, 724.3772.

4.2.6. 4,4′-Bis[bis(2,4,6-triisoprophylphenyl)phosphino]-3,3′,5,5′-tetramethylbiphenyl (*3a*)

To a solution of bis(2,4,6-triisopropylphenyl)(4′-bromo-3,3′,5′,5′-tetramethyl-4-biphenylyl)phosphine in tetrahydrofuran (15 mL) was added *t*-butyllitium (1.2 mL, 1.64 M in *n*-pentane) at −78 °C. After being stirred for 30 min, copper(I) chloride (120 mg, 1.21 mmol) was added to the reaction mixture at −78 °C. The mixture was gradually warmed to room temperature and stirred for 12 h. A solution of chlorobis(2,4,6-triisopropylphenyl)phosphine (451 mg, 0.954 mmol) in tetrahydrofuran (10 mL) was added to the reaction mixture at −78 °C and the mixture was refluxed for 24 h. After cooling to room temperature, *n*-hexane was added and the suspension was filtrated by Celite. The mixture was purified by column chromatography (SiO_2, *n*-hexane to *n*-hexane/ethyl acetate (20:1, v/v) and GPC (JAIGEL 1H + 2H, chloroform) to give **3a** (270 mg, 0.250 mmol, 27%).

3a: pale yellow solid; m.p. 200.0–202.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) δ 7.23 (4H, brs, arom.-2,2′,6,6′), 6.94 (4H, brs, arom.-3″,5″), 6.89 (4H, brs, arom.-3″,5″), 3.51 (4H, septet, $^3J_{HH}$ = 6.6 Hz, C*H*(CH$_3$)$_2$-2″,6″), 3.47 (4H, septet, $^3J_{HH}$ = 7.0 Hz, C*H*(CH$_3$)$_2$-2″,6″), 2.84 (4H, septet, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$-4″), 2.27 (6H, s, CH$_3$-3,3′ or 5,5′), 2.27 (6H, s, CH$_3$-3,3′ or 5,5′), 1.22 (24H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$-4″), 1.16 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$-2″,6″), 1.15 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$-2″,6″), 0.75 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$-2″,6″), 0.55 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$-2″,6″); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.75 (d, J_{PC} = 18.3 Hz, arom.-2″,6″), 152.86 (d, J_{PC} = 17.7 Hz, arom.-2″,6″), 149.35 (s, arom.-4″), 142.18 (d, J_{PC} = 18.9 Hz, arom.-3,3′,5,5′), 139.25 (s, arom.-1,1′), 139.09 (s, arom.-1,1′), 136.26 (d, (J_{PC} = 26.3 Hz, arom.-4,4′), 131.30 (d, J_{PC} = 19.4 Hz, arom.-1″), 126.77 (s, arom.-2,2′,6,6′), 122.18 (d, J_{PC} = 4.0 Hz, arom.-3″,5″), 121.95 (d, J_{PC} = 4.0 Hz, arom.-3″,5″), 34.04 (s, *C*H(CH$_3$)$_2$-4″), 32.16 (s, *C*H(CH$_3$)$_2$-2″,6″), 32.00 (s, *C*H(CH$_3$)$_2$-2″,6″), 24.53 (s, CH(*C*H$_3$)$_2$-2″,6″), 24.22 (s, CH(*C*H$_3$)$_2$-2″,6″), 23.90 (s, CH(*C*H$_3$)$_2$-4″), 23.72 (s, *C*H$_3$), 23.59 (s, CH(*C*H$_3$)$_2$-2″,6″), 22.77 (s, CH(*C*H$_3$)$_2$-2″,6″); ^{31}P NMR (81 MHz, $CDCl_3$, 295 K) δ −45.9 (s), −46.2 (s); FABMS *m*/*z* (rel. intensity) 1083 (M^+ + 1; 100), 233 (Tip^+; 35).

4.2.7. (4′-Bromo-3,3′,5,5′-tetraisopropyl-4-biphenylyl)-bis(2,4,6-triisopropylphenyl)phosphine (*6b*)

To a solution of **5b** (1.07 g, 2.24 mmol) in tetrahydrofuran (20 mL) was added *t*-butyllithium (4.23 mmol, 1.41 molL^{-1} in *n*-pentane) at −78 °C and the mixture was stirred for 30 min. Copper(I) chloride (270 mg, 2.71 mmol) was added and the mixture was gradually warmed and stirred for 5 h at 20 °C. A solution of chlorobis(2,4,6-triisopropylphenyl)phosphine (0.96 g, 2.04 mmol) in tetrahydrofuran (5 mL) was added at −78 °C and the mixture was gradually warmed and refluxed for 12 h. The mixture was concentrated under reduced pressure and purified by column chromatography (SiO_2/*n*-hexane: chloroform = 5:1, chloroform) to afford **6b** (320 mg, 0.38 mmol, 17%).

6b: yellow solid; m.p. 87.0–97.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 7.51 (2H, s, arom.-2′ or 6′), 7.24 (2H, d, $^4J_{PH}$ = 4.40 Hz, arom.-2,6), 6.91 (4H, d, $^4J_{PH}$ = 1.76 Hz, arom.-3″,5″), 6.90 (4H, d, $^4J_{PH}$ = 2.76 Hz, arom.-3″,5″), 3.52 (8H, sept, ^3J = 6.73 Hz, C*H*(CH$_3$)$_2$-3,5,3′,5′,2″, 6″), 2.82 (2H, sept,$^3J_{HH}$ = 6.73 Hz, C*H*(CH$_3$)$_2$-4″), 1.33–1.28 (18H, m, CH(C*H*$_3$)$_2$), 1.20 (12H, d, $^3J_{HH}$ = 6.80 Hz, CH(C*H*$_3$)$_2$), 1.16–1.14 (12H, m, CH(C*H*$_3$)$_2$), 0.76 (6H, d, $^3J_{HH}$ = 7.24 Hz, CH(C*H*$_3$)$_2$), 0.72 (6H, d, $^3J_{HH}$ = 7.20 Hz, CH(C*H*$_3$)$_2$), 0.65 (6H, d, $^3J_{HH}$ = 6.60 Hz, CH(C*H*$_3$)$_2$); ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) δ –1.2(s); FT-ICR-MS (ESI, positive). Found: *m*/*z* 836.5023. Calc. for $C_{54}H_{78}PBrH^+$: 836.5019 ([M + H]$^+$).

*4.2.8. 4,4′-Bis[bis(2,4,6-triisopropylphenyl)phosphino]-3,3′,5,5′-tetraisopropylbiphenyl (**3b**)*

To a solution of **6b** (0.35 g, 0.41 mmol) in tetrahydrofuran (10 mL) was added *t*-butyllithium (0.77 mmol, 1.40 mol L^{-1} in *n*-pentane) at −78 °C and the mixture was stirred for 30 min. Copper(I) chloride (40 mg, 0.37 mmol) was added and the mixture was gradually warmed and stirred for 20 h at 20 °C. A solution of chlorobis(2,4,6-triisopropylphenyl)phosphine (0.16 g, 0.34 mmol) in tetrahydrofuran (5 mL) was added at −78 °C and the mixture was gradually warmed and refluxed for 12 h. The mixture was concentrated under reduced pressure and purified by column chromatography (SiO_2/*n*-hexane: chloroform = 5:1, chloroform, ethyl acetate) and GPC (JAIGEL 1H + 2H/chloroform) to afford **3b** (60 mg, 0.53 mmol, 13%).

3b: yellow solid; m.p. 138–140 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 7.27 (4H, d, $^4J_{PH}$ = 2.19 Hz arom.-2,2′,6,6′), 6.91 (4H, d, $^4J_{PH}$ = 3.04 Hz, arom.-3″,5″), 6.90 (4H, d, $^4J_{PH}$ = 2.80 Hz, arom.-3″,5″), 3.50 (12H, m, C*H*$(CH_3)_2$-3,3′5,5′,2″, 6″), 2.82 (4H, sept, $^3J_{HH}$ = 6.85 Hz, C*H*$(CH_3)_2$-4″), 1.21 (36H, d, $^3J_{HH}$ = 6.85 Hz, CH(C*H*$_3$)$_2$-3,3′5,5′,2″, 6″), 1.17 (12H, d, $^3J_{HH}$ = 6.65 Hz, CH(C*H*$_3$)$_2$-4″), 1.14 (12H, d, $^3J_{HH}$ = 6.60 Hz, CH(C*H*$_3$)$_2$-4″), 0.77 (24H, d, $^3J_{HH}$ = 6.00 Hz, CH(C*H*$_3$)$_2$-3,3′5,5′,2″, 6″), 0.63 (12H, d, $^3J_{HH}$ = 6.50 Hz, CH(C*H*$_3$)$_2$-3,3′5,5′,2″, 6″); ^{13}C NMR (101 MHz, $CDCl_3$, 296 K) δ 153.59 (d, J_{PC} = 17.6 Hz, arom.-2″,6″), 153.58 (d, J_{PC} = 17.4 Hz, arom.-2″,6″), 153.37 (d, J_{PC} = 18.3 Hz, arom.-3,5), 149.66 (s, arom.-4″), 141.5 (s, arom.-1,1′), 134.93 (dd, J_{PC} = 26.7 Hz, J = 4.5 Hz, arom.-4,4′), 132.40 (d, J_{PC} = 33.2 Hz, arom.-1″), 122.59 (d, J_{PC} = 3.6 Hz, arom.-2,2′,6,6′), 122.45 (d, J_{PC} = 4.4 Hz, arom.-3″,5″), 122.35 (d, J_{PC} = 5.1 Hz, arom.-3″,5‴), 34.49 (s, *C*H$(CH_3)_2$-4″), 32.57 (d, J_{PC} = 12.0 Hz, *C*H$(CH_3)_2$-3,3′,5,5′), 32.43 (d, J_{PC} = 20.0 Hz, *C*H$(CH_3)_2$-2″,6″), 32.33 (d, J_{PC} = 24.0 Hz, *C*H$(CH_3)_2$-2″,6″), 25.07 (s, CH(*C*H$_3$)$_2$-4″), 24.94 (s, CH(*C*H$_3$)$_2$-4″), 24.48 (s, CH(*C*H$_3$)$_2$-3,3′,5,5′), 24.46 (s, CH(*C*H$_3$)$_2$-2″,6″), 23.90 (s, CH(*C*H$_3$)$_2$-4″), 23.48 (s, CH(*C*H$_3$)$_2$-3,3′,5,5′), 23.32 (s, CH(*C*H$_3$)$_2$-2″,6″); ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) δ −50.07 (s), −51.12 (s); FT-ICR-MS (ESI, positive). Found: *m*/*z* 1194.9185. Calc. for $C_{84}H_{124}P_2^+$: 1194.9173 ($[M]^+$).

*4.2.9. 3-(Dimesitylboryl)mesityl]bis(2,4,6-triisopropylphenyl)phosphine (**4a**).*

To a solution of bromo-3-(dimesitylboryl)mesitylene (521 mg, 1.17 mmol) in tetrahydrofuran (15 mL) was added *t*-butyllithium (2.33 mmol, 1.50 mol L^{-1} in *n*-pentane) at −78 °C and the mixture was stirred for 30 min. Copper(I) chloride (115 mg, 1.17 mmol) was added at −78 °C and the mixture was warmed to 15 °C and stirred for 3.5 h. A solution of chlorobis(2,4,6-triisopropylphenyl)phosphine (554 mg, 1.17 mmol) in tetrahydrofuran (5 mL) was added at −78 °C and the mixture was warmed to room temperature and refluxed for 12 h. The mixture was concentrated under reduced pressure and purified by column chromatography (Al_2O_3/*n*-hexane) and GPC (JAIGEL 1H + 2H/toluene) to afford **4a** (243 mg, 0.30 mmol, 26%).

4a: bright yellow solid; m.p. 195–197 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 6.91 (s, 1H, arom.), 6.86 (s, 2H, arom.), 6.80 (s, 1H, arom.), 6.77 (s, 1H, arom.), 6.73 (s, 2H, arom.), 6.66 (s, 1H, arom.), 6.64 (s, 1H, arom.), 3.56–3.33 (4H, m, C*H*$(CH_3)_2$-2,6), 2.82 (1H, sept, J = 6.86 Hz, C*H*$(CH_3)_2$-4), 2.81 (1H, sept, J = 6.86 Hz, C*H*$(CH_3)_2$-4), 2.27 (3H, CH_3), 2.24 (3H, CH_3), 2.20 (3H, CH_3), 2.19 (3H, CH_3), 2.14 (3H, CH_3), 1.99 (3H, CH_3), 1.97 (3H, CH_3), 1.92 (3H, CH_3), 1.91 (3H, CH_3), 1.21 (12H, d, J = 6.89 Hz, CH(C*H*$_3$)$_2$-4), 1.18 (3H, d, J = 6.91 Hz, CH(C*H*$_3$)$_2$-2,6), 1.11 (3H, d, J = 6.33 Hz, CH(C*H*$_3$)$_2$-2,6), 1.10 (3H, d, J = 6.37 Hz, CH(C*H*$_3$)$_2$-2,6), 1.02 (3H, d, J = 6.62 Hz, CH(C*H*$_3$)$_2$-2,6), 0.80 (3H, d, J = 6.56 Hz, CH(C*H*$_3$)$_2$-2,6), 0.72 (3H, d, J = 6.51 Hz, CH(C*H*$_3$)$_2$-2,6), 0.47 (3H, d, J = 6.56 Hz, CH(C*H*$_3$)$_2$-2,6), 0.42 (3H, d, J = 6.35 Hz, CH(C*H*$_3$)$_2$-2,6); ^{13}C NMR (101 MHz, $CDCl_3$, 296 K) δ 153.98 (d, J = 22.14 Hz, arom. (Tip)-2,6), 153.53 (d, J = 14.83 Hz, arom.(Tip)-2,6), 152.86 (d, J = 20.52 Hz, arom.(Tip)-2,6), 152.14 (d, J = 13.77 Hz, arom.(Tip)-2,6), 149.10 (s, arom.(Tip)-4), 149.04 (s, arom.(Tip)-4), 146.69 (s, arom.-3), 144.41 (brs, arom.(Mes)-1), 144.24 (brs, arom.(Mes)-1), 143.09 (d, J = 14.34 Hz, arom.(Mes)-2,6), 143.04 (d, J = 22.90 Hz, arom.(Mes)-2,6), 140.91 (s, arom.(Me*C*)), 140.78 (s, arom.(Me*C*)), 140.60 (s, arom.(Me*C*)), 140.34 (s, arom.(Me*C*)), 139.40 (s, arom.(Me*C*)), 139.23 (s, arom.(Me*C*)), 138.91 (s, arom.(Me*C*)), 135.26 (d, J = 27.03 Hz, arom.-1), 132.33 (d, J = 20.61 Hz, arom. (Tip)-1), 131.46 (d, J = 19.38 Hz, arom.(Tip)-1), 131.11 (d, J = 4.07 Hz, arom.(Mes)-5), 128.73 (s, arom.(Mes)-3,5), 128.69 (s, arom.(Mes)-3,5), 128.54 (s, arom.(Mes)-3,5), 122.38 (d, J = 3.68 Hz, arom.(Tip)-3,5), 122.14 (d, J = 4.68 Hz, arom.(Tip)-3,5), 121.92 (d, J = 2.76 Hz, arom.(Tip)-3,5), 121.46 (d, J = 5.23 Hz, arom.(Tip)-3,5), 34.03 (s, *C*H$(CH_3)_2$-4), 33.96 (s, *C*H$(CH_3)_2$-4), 32.41 (d, J = 15.63 Hz, *C*H$(CH_3)_2$-2,6), 31.97-31.66 (d × 3, *C*H$(CH_3)_2$-2,6), 24.69–21.16 (*C*H$(CH_3)_2$ and CH_3); ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) δ −46.6 (s), −47.4 (s); UV–Vis (CH_2Cl_2, $c = 4.15 \times 10^{-5}$ mol L^{-1}) λ_{max}(log ε)/nm 330 (4.22); FT-ICR-MS (ESI, positive). Found: 805.6017. Calc. for $C_{57}H_{78}BPH^+$: 805.6007 ($[M + H]^+$).

*4.2.10. [4-(Dimesitylboryl)duryl]bis(2,4,6-triisopropylphenyl)phosphine (**4b**)*

To a solution of bromo-4-(dimesitylboryl)durene (502 mg, 1.09 mmol) in tetrahydrofuran (15 mL) was added *t*-butyllithium (2.16 mmol, 1.50 mol L^{-1} in *n*-pentane) at −78 °C and the mixture was stirred for 30 min.

Copper(I) chloride (107 mg, 1.08 mmol) was added at −78 °C and the mixture was warmed to 15 °C and stirred for 3.5 h. A solution of chlorobis(2,4,6-triisopropylphenyl)phosphine (518 mg, 1.09 mmol) in tetrahydrofuran (5 mL) was added at −78 °C and the mixture was warmed to room temperature and refluxed for 36 h. The mixture was concentrated under reduced pressure and purified by column chromatography (Al_2O_3/*n*-hexane) and GPC (JAIGEL 1H + 2H/toluene) to afford **4b** (217 mg, 0.26 mmol, 24%).

4b: bright yellow solid; m.p. 98–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 6.92 (2H, brs, Tip-3,5), 6.90 (2H, d, J = 2.39 Hz, Tip-3,5), 6.74 (4H, brs, Mes-3,5), 3.54 (4H, brs, C*H*(CH_3)$_2$-2,6), 2.84 (2H, sept, J = 6.88 Hz, C*H*(CH_3)$_2$-4), 2.27 (6H, s, CH_3), 2.12 (3H, brs, CH_3), 2.09 (3H, brs, CH_3), 2.10 (6H, s, CH_3), 1.96 (6H, s, CH_3), 1.94 (6H, s, CH_3), 1.27 (6H, brs, CH(C*H*$_3$)$_2$-2,6), 1.23 (12H, d, $^3J_{HH}$ = 6.91 Hz, CH(C*H*$_3$)$_2$-4), 1.14 (6H, brs, CH(C*H*$_3$)$_2$-2,6), 0.70 (6H, d, $^3J_{HH}$ = 6.33 Hz, CH(C*H*$_3$)$_2$-2,6), 0.64 ((6H, d, $^3J_{HH}$ = 6.05 Hz, CH(C*H*$_3$)$_2$-2,6); ^{13}C NMR (101 MHz, $CDCl_3$, 296 K) δ 153.46 (d, J_{PC} = 17.8 Hz, arom.(Tip)-2,6), 152.45 (d, J_{PC} = 17.4 Hz, arom.-(Tip)-2,6), 149.05 (s, arom.(Tip)-4), 148.40 (brs, arom.-4), 144.65 (brs, arom.(Mes)-1), 140.97 (s, arom.(Mes)-2,6), 140.85 (s, arom.(Mes)-2,6), 140.74 (s, arom.(Mes)-2,6), 139.67 (d, J = 25.23 Hz, arom.-1), 137.41 (d, J = 19.2 Hz, arom.-2,6), 135.36 (d, J = 3.89 Hz, arom.-3,5), 135.14 (d, J = 3.48 Hz, arom.-3,5), 132.11 (d, J = 21.2 Hz, arom.(Tip)-1), 128.80 (s, arom.(Mes)-3,5), 128.69 (s, arom.(Mes)-3,5), 122.19 (d, J = 4.3 Hz, arom.(Tip)-3,5), 121.83 (d, J = 4.0 Hz, arom.(Tip)-3,5), 34.04 (s, *C*H(CH_3)$_2$-4), 32.00 (d, J = 18.2 Hz, *C*H(CH_3)$_2$-2,6), 31.50 (d, J = 17.0 Hz, *C*H(CH_3)$_2$-2,6), 24.42 (d, J = 21.4 Hz, *C*H_3-2,6), 23.91 (s, CH(*C*H_3)$_2$-4), 23.65 (s), 23.23 (s), 22.76 (s), 21.20 (s), 20.59 (s), 19.87 (s), 19.69 (s); ^{31}P NMR (162 MHz, $CDCl_3$, 296 K) δ −42.1 (s), −42.5 (s); UV–Vis (CH_2Cl_2, $c = 4.15 \times 10^{-5}$ mol L^{-1}) λ_{max} (log ε)/nm 324 (3.96), 385 (3.29); FT-ICR-MS (ESI). Found: 819.6182. Calc. for $C_{58}H_{80}BPH^+$: 819.6163 ([M + H]$^+$).

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