Tris[tri(2-thienyl)phosphine]palladium as the Catalyst Precursor for Thiophene-Based Suzuki-Miyaura Crosscoupling and Polycondensation

WEIWEI LI,1 YANG HAN,1 BINSONG LI,1 CAIMING LIU,2 ZHISHAN BO1

1State Key Laboratory of Polymer Physics and Chemistry, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

2CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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INTRODUCTION

Oligo and polythiophenes and their derivatives, which exhibited very high carrier mobility in films, have attracted considerable attention due to their applications in the fields of photovoltaics,1–3 light-emitting diodes,4 and thin film transistors.5 The regioregularity and the molecular weight of polythiophene play crucial roles in the fabrication of efficient organic solar cells.6–8 In the literature, the synthetic strategies for the preparation of regioregular polythiophenes mainly involved Kumada-Corriu,9,10 Rieke (also called Negishi),11,12 Stille,13,14 and Suzuki15–18 crosscoupling reactions. However, for Kumada-Corriu and Rieke crosscoupling reactions, the monomers (Grignard reagents or organozinc compounds) are very susceptible and not compatible with functional groups such as aldehyde, carboxylic ester, etc.; for Stille crosscoupling, the organotin-based monomers are highly toxic.

Suzuki polycondensation (SPC) route has many advantages, such as wide functional group tolerance, the nontoxic, stable, and easy purification of monomers, etc. however, it failed to achieve access to high-molecular-weight regioregular polythiophene.15–18 Recently, electron-rich and bulky phosphorus ligands have been welldeveloped, which show high activity even in the coupling of electron-rich and hindered aryl chloride substrates.19–23 However, the use of a single ligand to satisfy the diverse requirements of different Suzuki-Miyaura couplings remains unrealized.19 The employment of such ligands in Suzuki-Miyaura coupling of thiophene-based compounds did not give results as good as the coupling of other aryl-based substrates.22 Here, we describe the use of a novel efficient catalyst

**EXPERIMENTAL**

**Materials and Instruments**

All chemicals were purchased from commercial suppliers and used without further purification. Solvents were dried according to standard procedures. 3-hexylthiophene,24 2,5-dibromo-3-hexylthiophene,25 5-bromothiophene-2-carbaldehyde,26 2-(5-bromo-4-ethyl-2-thienyl)4,4,5,5-tetramethyl-1,3-dioxaborolane (3),16 and 2-(5-bromo-4-ethyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)17 were prepared according to literature procedures. All reactions were performed under an atmosphere of nitrogen and monitored by TLC with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200–300 mesh).1H, 13C, and 31P NMR spectra were recorded on a Bruker DM 300 or AV 400 spectrometer in CDCl3. The gel permeation chromatography (GPC) measurements were performed on a Waters chromatography connected to a Waters 410 differential refractometer with THF as an eluent. Elemental analyses were performed on a Flash EA 1112 analyzer.

**Synthesis of Tris[tri(2-thienyl)phosphine] palladium(0) [Pd(PTh3)3]**

A degassed mixture of PdCl2 (0.05 g, 0.28 mmol) and tri(2-thienyl)phosphine (0.30 g, 1.07 mmol) in DMF (11 mL) was heated to 90 °C and then hydrazine hydrate (0.13 mL, 0.28 mmol) was added over 1 min. The dark solution was allowed to cool to room temperature. The crystals were collected by filtration and washed successively with ethanol and ether. Pd(PTh3)3 was obtained as a yellow crystal.

$^1$H-NMR (400 MHz, CDCl3) δ 7.42 (d, 3H), 7.15 (m, 3H), 6.88 (t, 3H). 13C-NMR (400 MHz, CDCl3) δ 185.54, 142.35, 129.41, 117.90, 87.75. Anal. Calcd. for C36H27P3-PdS9: C, 45.63; H, 2.87. Found: C, 45.62; H, 2.89.

Crystal data of Pd(PTh3)3 (C36H27P3PdS9): $M_w$ = 947.43. T = 293(2) K. Rhombohedra, space group R3, $a = 20.419(3)$, $b = 20.419(3)$, $c = 16.717(3)$ A, $x = 90°$, $\beta = 90°$, $\gamma = 120°$. V = 6036.1(17) A3, Z = 6, $D_\text{calc} = 1.564$ mg m$^{-3}$, $\mu = 1.074$ mm$^{-1}$, R1 = 0.1010, wR2 = 0.2029 (all data), GOF = 0.989.

**5-Bromo-2-iodothiophene-3-carbaldehyde**

To a degassed solution of 5-bromothiophene-3-carbaldehyde (3.0 g, 15.7 mmol) in chloroform (100 mL) and acetic acid (20 mL), which was cooled to 0–5 °C with an ice-water bath, was added N-iodosuccinimide (5 g, 22.2 mmol). The ice-water bath was removed and the resulted mixture was stirred at room temperature for 4 h. The deep red solution was poured into an aqueous Na2SO3 solution, the organic layer was separated, the aqueous layer was extracted with chloroform, and the combined organic layers were dried over anhydrous Na2SO4 and evaporated to dryness. The crude product was chromatographically purified on silica gel eluting with hexane/CH2Cl2 (1:1) to give 5-bromo-2-iodothiophene-3-carbaldehyde as a yellow solid (4.80 g, 96%).

$^1$H-NMR (400 MHz, CDCl3) δ 9.54 (s, 1H), 7.27 (s, 1H). 13C-NMR (400 MHz, CDCl3) δ 185.54, 142.35, 129.41, 117.90, 87.75. Anal. Calcd. for C5H2BrOS: C, 18.95; H, 0.64; S, 10.32. Found: C, 18.91; H, 0.30; S, 10.12.

**3,4-Bis(4-octyloxyphenyl)-2,5-dibromothiophene**

To a degassed solution of 3,4-bis(4-octyloxyphe nyl)thiophene (0.51 g, 1.03 mmol) in chloroform (100 mL), which was cooled to 0–5 °C with an ice-water bath, N-bromosuccinimide (0.52 g, 2.9 mmol) was added. The ice-water bath was removed and the resulted mixture was stirred at room temperature for 4 h. The deep red solution was poured into an aqueous Na2SO3 solution, the organic layer was separated, the aqueous layer was extracted with chloroform, and the combined organic layers were dried over anhydrous Na2SO4 and evaporated to dryness. The crude product was chromatographically purified on silica gel eluting with hexane/CH2Cl2 (2:1) to give 3,4-bis(4-octyloxyphe nyl)-2,5-dibromothiophene as a yellow solid (0.66 g, 100%).

$^1$H-NMR (400 MHz, CDCl3) δ 6.96 (d, 4H), 6.76 (d, 4H), 3.90 (t, 4H), 1.75 (m, 4H), 1.4 (m, 20 H), 0.88 (t, 6H). 13C-NMR (400 MHz, CDCl3) δ 158.49, 141.93, 131.28, 126.61, 113.88, 108.87, 76.85, 31.77, 29.32, 29.25, 29.19, 26.03, 22.61, 14.04. Anal. Calcd. for C32H22Br2O2S: C, 59.08; H, 6.51; S, 4.77. Found: C, 58.78; H, 6.49; S, 4.93.
5-(Thiophen-2-yl)thiophene-2-carbaldehyde

by Pd(PPh3)4

A mixture of 5-bromothiophene-2-carbaldehyde (0.1260 g, 0.659 mmol), 2-thiopheneboronic ester (0.1384 g, 0.659 mmol), THF (20 mL), water (5 mL), NaHCO3 (1.1 g, 13.2 mmol) and Pd(PPh3)4 (11.4 mg, 9.93 × 10^{-3} mmol) was carefully degassed and charged with nitrogen (Table 1, Entry 1). The reaction mixture was stirred and refluxed for 48 h. CH2Cl2 was then added, and the organic layer was separated and dried over Na2SO4. The crude product was chromatographically purified on silica gel eluting with hexane/CH2Cl2 (1:2) to provide the title compound as a yellow solid (84 mg, 66%).

1H-NMR (400 MHz, CDCl3) δ 9.86 (s, 1H), 7.67 (d, 1H), 7.36 (d, 2H), 7.25 (d, 1H), 7.08 (t, 1H). 13C-NMR (400 MHz, CDCl3) δ 182.50, 147.14, 141.70, 137.25, 136.02, 128.33, 127.06, 126.12, 124.21. Anal. Calcd. for C9H6O2S2: C, 55.64; H, 3.11; S, 32.04. Found: C, 55.40; H, 3.19; S, 33.01.

5-(Thiophen-2-yl)thiophene-2-carbaldehyde

by Pd(PTh3)3

A mixture of 5-bromothiophene-2-carbaldehyde (0.1665 g, 0.871 mmol), 2-thiopheneboronic ester (0.183 g, 0.871 mmol), THF (20 mL), water (5 mL), NaHCO3 (1.46 g, 17.4 mmol), and Pd(PTh3)3 (12.4 mg, 1.31 × 10^{-2} mmol) was carefully degassed and charged with nitrogen (Table 1, Entry 1). The reaction mixture was stirred and refluxed for 48 h under N2. CH2Cl2 was then added, and the organic layer was separated and dried over Na2SO4. The crude product was chromatographically purified on silica gel eluting with hexane/CH2Cl2 (1:2) to provide the title compound as a yellow solid (104 mg, 67%).

1H-NMR (400 MHz, CDCl3) δ 9.87 (s, 1H), 7.67 (d, 1H), 7.36 (d, 2H), 7.25 (d, 1H), 7.08 (t, 1H). 13C-NMR (400 MHz, CDCl3) δ 182.50, 147.14, 141.70, 137.25, 136.02, 128.33, 127.06, 126.12, 124.21. Anal. Calcd. for C9H6O2S2: C, 55.64; H, 3.11; S, 32.04. Found: C, 55.60; H, 3.19; S, 33.01.

Table 1. Suzuki-Miyaura Coupling of Thienyl Halide and Thiophene-2-Boronic Ester with Pd(PPh3)4 or Pd(PTh3)3 as the Catalyst Precursor

<table>
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<tr>
<th>Entry</th>
<th>Thienyl Halide</th>
<th>Product</th>
<th>Pd(PPh3)4</th>
<th>Pd(PTh3)3</th>
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<td><img src="https://example.com/image2.png" alt="Image" /></td>
<td>66</td>
<td>95</td>
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<tr>
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<td>82</td>
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<td>78</td>
</tr>
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<td><img src="https://example.com/image10.png" alt="Image" /></td>
<td>77</td>
<td>96</td>
</tr>
</tbody>
</table>

*a* 1 equiv of thienyl halide, 1 equiv of thiophene boronic ester, 20 equiv of NaHCO3, THF (20 mL), H2O (5 mL), 1.5 mol % equiv of Pd(PPh3)4, or Pd(PTh3)3, and reflux for 48 h.

*b* 1 equiv of thienyl halide, 2 equiv of thiophene boronic ester, 20 equiv of NaHCO3, THF (20 mL), H2O (5 mL), 1.5 mol % equiv of Pd(PPh3)4, or Pd(PTh3)3, and reflux for 48 h.

*c* 1 equiv of thienyl halide, 1 equiv of thiophene boronic ester, 20 equiv of NaHCO3, THF (20 mL), H2O (5 mL), 1.5 mol % equiv of Pd(PPh3)4, or Pd(PTh3)3, and 50 °C for 48 h.
with hexane/CH$_2$Cl$_2$ (1:2) to provide 5-(2-thiophenyl)thiophene-2-carbaldehyde as a yellow solid (0.161 g, 95%).

2,5-Dithienyl-3-hexylthiophene by Pd(PPh$_3$)$_4$

A mixture of 2,5-dibromo-3-hexylthiophene (0.1566 g, 0.481 mmol), 2-thiopheneboronic ester (0.2020 g, 0.962 mmol), THF (20 mL), water (5 mL), NaHCO$_3$ (0.81 g, 9.62 mmol), and Pd(PPh$_3$)$_4$ (10.7 mg, 7.2 $\times$ 10$^{-3}$ mmol) was carefully degassed and charged with nitrogen (Table 1, Entry 2). The reaction mixture was stirred and refluxed for 48 h. CH$_2$Cl$_2$ was then added, the organic layer separated, and dried over Na$_2$SO$_4$. The crude product was chromatographically purified on silica gel eluting with hexane to provide the title compound as a green oil (0.121 g, 76%).

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 (d, 1H), 7.18 (d, 1H), 7.15 (d, 1H), 7.05 (t, 1H), 7.00 (m, 2H). $^{13}$C-NMR (400 MHz, CDCl$_3$) $\delta$ 140.27, 137.22, 135.88, 135.09, 129.51, 127.81, 127.38, 126.49, 125.82, 125.29, 124.28, 123.53, 31.63, 30.53, 29.31, 29.20, 22.60, 14.07. Anal. Calcd. for C$_{18}$H$_{20}$S$_3$: C, 65.01; H, 6.06; S, 29.01. Found: C, 64.85; H, 6.09; S, 28.93.

2,5-Dithienyl-3-hexylthiophene by Pd(PTh$_3$)$_3$

A mixture of 2,5-dibromo-3-hexylthiophene (0.1568 g, 0.481 mmol), 2-thiopheneboronic ester (0.2178 g, 0.962 mmol), THF (20 mL), water (5 mL), NaHCO$_3$ (0.871 g, 10.4 mmol), and Pd(PTh$_3$)$_3$ (7.36 mg, 7.8 $\times$ 10$^{-3}$ mmol) was carefully degassed and charged with nitrogen (Table 1, Entry 2). The reaction mixture was stirred and refluxed for 48 h under N$_2$. CH$_2$Cl$_2$ was then added; and the organic layer was separated, dried over Na$_2$SO$_4$, and evaporated to dryness. The crude product was chromatographically purified on silica gel eluting with hexane to provide the title compound as a green oil (0.141 g, 82%).

3,4-Bis(4-octyloxyphenyl)-2,5-di(2-thienyl)thiophene by Pd(PPh$_3$)$_4$

A mixture of 3,4-bis(4-octyloxyphenyl)-2,5-dibromothiophene (0.1003 g, 0.154 mmol), 2-thiopheneboronic ester (64.8 mg, 0.308 mmol), THF (18 mL), water (4 mL), NaHCO$_3$ (1 g, 11.9 mmol), and Pd(PPh$_3$)$_4$ (2.7 mg, 2.3 $\times$ 10$^{-3}$ mmol) was carefully degassed and charged with nitrogen (Table 1, Entry 3). The reaction mixture was stirred and refluxed for 48 h. CH$_2$Cl$_2$ was then added, the organic layer separated, and dried over Na$_2$SO$_4$. The crude product was chromatographically purified on silica gel eluting with hexane/CH$_2$Cl$_2$ (1:1) to provide the title compound as a yellow solid (95 mg, 54%).

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.23 (d, 1H), 7.11 (d, 1H), 7.01 (t, 1H), 6.97 (d, 1H), 6.92 (d, 1H). Anal. Calcd. for C$_{40}$H$_{48}$O$_2$S$_3$: C, 73.12; H, 7.36; S, 14.64. Found: C, 72.90; H, 7.38; S, 14.64.

3,4-Bis(4-octyloxyphenyl)-2,5-di(2-thienyl)thiophene by Pd(PTh$_3$)$_3$

A mixture of 3,4-bis(4-octyloxyphenyl)-2,5-dibromothiophene (0.1399 g, 0.215 mmol), 2-thiopheneboronic ester (90.36 mg, 0.431 mmol), THF (20 mL), water (5 mL), NaHCO$_3$ (1 g, 11.9 mmol), and Pd(PTh$_3$)$_3$ (3.1 mg, 3.23 $\times$ 10$^{-3}$ mmol) was carefully degassed and charged with nitrogen (Table 1, Entry 3). The reaction mixture was stirred and refluxed for 48 h. CH$_2$Cl$_2$ was then added; and the organic layer was separated, dried over Na$_2$SO$_4$, and evaporated to dryness. The crude product was chromatographically purified on silica gel eluting with hexane/CH$_2$Cl$_2$ (1:1) to provide the title compound as a yellow solid (0.129 g, 92%).

2-Bromo-5-thienyl-thiophene by Pd(PPh$_3$)$_4$

A mixture of 2-bromo-5-iodothiophene (0.2072 g, 0.717 mmol), 2-thiopheneboronic ester (0.1506 g, 0.717 mmol), THF (20 mL), water (5 mL), NaHCO$_3$ (1.21 g, 14.3 mmol), and Pd(PPh$_3$)$_4$ (12.4 mg, 1.08 $\times$ 10$^{-2}$ mmol) was carefully degassed and charged with nitrogen (Table 1, Entry 4). The reaction mixture was stirred and refluxed for 48 h. CH$_2$Cl$_2$ was then added, the organic layer separated, and dried over Na$_2$SO$_4$. The crude product was chromatographically purified on silica gel eluting with hexane to provide the title compound as a yellow solid (95 mg, 54%).

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.23 (d, 1H), 7.11 (d, 1H), 7.01 (t, 1H), 6.97 (d, 1H), 6.92 (d, 1H). Anal. Calcd. for C$_8$H$_5$BrS$_2$: C, 39.19; H, 2.06; S, 25.63. Found: C, 39.21; H, 2.14; S, 26.16.
2-Bromo-5-thienyl-thiophene by Pd(PTh3)3
A mixture of 2-bromo-5-iodothiophene (0.21 g, 0.727 mmol), 2-thiopheneboronic ester (0.1527 g, 0.727 mmol), THF (20 mL), water (5 mL), NaHCO3 (1.22 g, 14.5 mmol), and Pd(PTh3)3 (10.3 mg, 10.9 × 10−3 mmol) was carefully degassed and charged with nitrogen (Table 1, Entry 4). The reaction mixture was stirred and refluxed for 48 h. CH2Cl2 was then added, the organic layer separated, and dried over Na2SO4. The crude product was chromatographically purified on silica gel eluting with hexane to provide the title compound as a yellow solid (0.139 g, 78%).

5-Bromo-2-thienyl-thiophene-3-carbaldehyde by Pd(PPh3)4
A mixture of 5-bromo-2-iodothiophene-3-carbaldehyde (0.1935 g, 0.610 mmol), 2-thiopheneboronic ester (0.128 g, 0.61 mmol), THF (20 mL), water (5 mL), NaHCO3 (1.03 g, 12.2 mmol), and Pd(PPh3)4 (10.6 mg, 9.15 × 10−3 mmol) was carefully degassed and charged with nitrogen (Table 1, Entry 5). The reaction mixture was stirred and refluxed for 48 h under N2. CH2Cl2 was added; the organic layer was separated, dried over Na2SO4, and evaporated to dryness. The crude product was chromatographically purified on silica gel eluting with hexane/CH2Cl2 (2:5) to provide the title compound as a yellow solid (0.128 g, 77%).

5-Bromo-2-(2-thienyl)thiophene-3-carbaldehyde by Pd(PTh3)3
A mixture of 5-bromo-2-iodothiophene-3-carbaldehyde (0.196 g, 0.617 mmol), 2-thiopheneboronic ester (0.1296 g, 0.617 mmol), THF (20 mL), water (5 mL), NaHCO3 (1.04 g, 12.3 mmol), and Pd(PTh3)3 (8.8 mg, 9.26 × 10−3 mmol) was carefully degassed and charged with nitrogen (Table 1, Entry 5). The reaction mixture was stirred and refluxed for 48 h. CH2Cl2 was then added, the organic layer separated, and dried over Na2SO4. The crude product was chromatographically purified on silica gel eluting with hexane/CH2Cl2 (2:5) to provide the title compound as a yellow solid (0.163 g, 96%).

General Procedures for the Preparation of P3HT
A mixture of monomer 3 or 4, THF or THF/Toluene, water, NaHCO3 and the catalyst precursor (Pd(PPh3)4 or Pd(PTh3)3) was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 3 days. CHCl3 and aqueous hydrochloric acid was then added; the organic layer was separated and dried over Na2SO4. After the removal of the solvent, the residue was dissolved in a minimum amount of THF and precipitated into methanol. The formed deep red precipitates were collected by filtration and further purified by extraction with methanol, hexane, and THF successively. The THF extraction was collected and evaporated to dryness, and the residue was dissolved in a small amount of benzene and freeze-dried to give P3HT as a dark solid.

1H-NMR (400 MHz, CDCl3) δ 6.98 (s, 1H), 2.80 (b, 2H), 1.70 (b, 2H), 1.45–1.2 (b, 6H), 0.90 (b, 3H). The product was characterized with a head to tail linkage of 97% ± 1% by 1H-NMR integration.

Entry 1: 3 (0.16 g, 0.36 mmol), THF (12 mL), H2O (3.5 mL), NaHCO3 (0.59 g, 7 mmol) and Pd(PTh3)3 (4.3 mg, 4.5 × 10−3 mmol) were used. 42 mg (a yield of 72%) of P3HT (THF fraction) was obtained.

Entry 2: 3 (0.16 g, 0.38 mmol), THF (8 mL), Toluene (2 mL), H2O (3.5 mL), NaHCO3 (0.65 g, 7.7 mmol) and Pd(PTh3)3 (4.8 mg, 5.1 × 10−3 mmol) were used. 44 mg (a yield of 68%) of P3HT (THF fraction) was obtained.

Entry 3: 3 (0.21 g, 0.40 mmol), THF (7 mL), Toluene (7 mL), H2O (4 mL), NaHCO3 (0.84 g, 10 mmol) and Pd(PTh3)3 (6.1 mg, 6.4 × 10−3 mmol) were used. 52 mg (a yield of 62%) of P3HT (THF fraction) was obtained.

Entry 4: 4 (0.19 g, 0.51 mmol), THF (18 mL), H2O (4.5 mL), NaHCO3 (0.84 g, 10 mmol) and Pd(PTh3)3 (5.8 mg, 6.1 × 10−3 mmol) was used. 17 mg (a yield of 20%) of P3HT (THF fraction) was obtained.

Entry 5: 4 (0.15 g, 0.40 mmol), THF (8 mL), Toluene (2 mL), H2O (3.5 mL), NaHCO3 (0.67 g, 8.0 mmol) and Pd(PTh3)3 (4.6 mg, 4.9 × 10−3 mmol) was used. 18 mg (a yield of 30%) of P3HT (THF fraction) was obtained.

Entry 6: 4 (0.14 g, 0.38 mmol), THF (7 mL), Toluene (7 mL), H₂O (3 mL), NaHCO₃ (0.65 g, 7.7 mmol) and Pd(PTh₃)₃ (4.5 mg, 4.7 × 10⁻³ mmol) was used. 18 mg (a yield of 27%) of P3HT (THF fraction) was obtained.

Entry 7: 3 (0.18 g, 0.43 mmol), THF (18 mL), H₂O (4 mL), NaHCO₃ (0.72 g, 8.57 mmol) and Pd(PPh₃)₄ (5.0 mg, 4.3 × 10⁻³ mmol) was used. 15 mg (a yield of 22%) of P3HT (THF fraction) was obtained.

Entry 8: 4 (0.18 g, 0.48 mmol), THF (18 mL), H₂O (4 mL), NaHCO₃ (0.81 g, 9.6 mmol), and Pd(PPh₃)₄ (5.6 mg, 4.8 × 10⁻³ mmol) were used. 9 mg (a yield of 11%) of P3HT (THF fraction) was obtained.

RESULTS AND DISCUSSION

Suzuki-Miyaura Crosscoupling of Thiophene-Based Monomers

The preparation of zerovalent palladium complex of tri(2-thienyl)phosphine is similar to the procedure reported for Pd(PPh₃)₄. X-ray crystallography and computational chemistry finally revealed that each zerovalent palladium atom has three tri(2-thienyl)phosphine ligands in this complex. The ORTEP diagram of Pd(PTh₃)₃ is given in Figure 1. The length of the Pd(0)-phosphine bond in Pd(PTh₃)₃ is 2.2849 Å, smaller than that of Pd(0)-phosphine (2.427, 2.458 Å) in Pd(PPh₃)₄.

The well-known catalytic cycle of the Suzuki-Miyaura crosscoupling reaction includes three key steps: oxidative addition, transmetalation, and reductive elimination, in which oxidative addition is the rate-determining step. In general, palladium complexes with fewer than four phosphine ligands or bulky phosphines are highly reactive in the oxidative addition step because of the ready formation of coordinately unsaturated palladium species, and the electron-donating ability of ligands is usually considered to be an important factor in improving the activity of the catalyst. The electron-rich ligands facilitate the oxidative addition by increasing the electron-density of the palladium intermediate. The ligand–ligand exchange reaction between aryls at a Pd center and the phosphorus of the ligand and the deboronation of the thiophene-based monomers are the main side reactions that prohibit the formation of high-molecular-weight polythiophenes.

The use of electron-rich compounds as a ligand of palladium for Suzuki polycondensation should suppress the side reactions and afford higher molecular weight polymers.

According to the report of Katritzky et al., furyl and thiényl ring systems are stronger electron donors than unsubstituted phenyl rings. Triphenylphosphine and tri(2-furyl)phosphine are well-known ligands for zerovalent palladium compounds. While TFP has proven highly efficient for Stille, Negishi and Heck reactions, TFP is yet to be proven as effective for the Suzuki-Miyaura couplings. To the best of our knowledge, this is the first report on tri(2-thienyl)phosphine as a ligand of zerovalent palladium for catalyzing coupling reactions. The high activity of the tri(2-thienyl)phosphine ligand in Suzuki-Miyaura coupling of thiophene-based substrates is probably due to the strong electron donating ability of the thienyl rings.

This tri(2-thienyl)phosphine-based zerovalent palladium complex was firstly used as the catalyst precursor to screen Suzuki-Miyaura cross-coupling of thiophene-based substrates. The results are summarized in Table 1. For comparison, the results of Pd(PPh₃)₄ as a catalyst precursor are also listed in Table 1. Under the same reaction conditions, Pd(PTh₃)₃ gave better results than the traditional Pd(PPh₃)₄ did. Table 1 clearly demonstrates that the coupling of
thiophene-based substrates carrying aldehyde functional groups gives improved yields.

Suzuki-Miyaura Polycondensation

To evaluate the catalytic activity in polymerization, the freshly prepared catalyst precursor, Pd(PTh$_3$)$_3$, was applied in the Suzuki polycondensation of the thiophene-based monomers. AB-type monomers 3-hexyl-5-iodothiophene-2-boronic pinacol ester (3) and 3-hexyl-5-bromo-thiophene-2-boronic pinacol ester (4) were used for the polymerization (Scheme 1). The reactions were carried out in a biphasic mixture of aqueous NaHCO$_3$/THF or aqueous NaHCO$_3$/THF/toluene with approximate 1.2 mol % of Pd(PPh$_3$)$_4$ or Pd(PTh$_3$)$_3$ as catalyst precursor. Standard workup afforded P3HT as a dark-red amorphous material and the results are summarized in Table 2. The molecular weights of entries 1–8 were as determined by GPC calibrated with polystyrene standard. The head-to-tail regularity of P3HT is over 97% determined by the integration of $^1$H-NMR spectra following a literature method. Table 2 illustrates (a) the use of Pd(PTh$_3$)$_3$ instead of Pd(PPh$_3$)$_4$ as a catalyst precursor in SPC of both iodo- and bromo-substituted thiophene monomers can significantly boost the yields and molecular weights of the polymers; (b) the combination of iodo monomer 3 and Pd(PTh$_3$)$_3$ as a catalyst precursor leads to a yield of 72% and weight average molecular weight of 26,000 for P3HT. In comparison to the literature reported results of the polymerization of 3-alkyl-5-bromothiophene-2-boronic pinacol ester with t-Bu$_3$P and Buchwald-type ligands (Chart 1) as the ligands of palladium, our results (Table 2, Entries 5 and 6) are comparable. Tri(2-thienyl)phosphine ligand is slightly superior to t-Bu$_3$P, (o-biphenyl)P$^t$Bu$_2$, and 5, but slightly inferior to ligand 6. It is worth to note that the synthesis of tri(2-thienyl)phosphine ligand is much simpler than the preparation of Buchwald-type ligands. The use of phosphorus ligand-free palladium catalyst, Pd(OAc)$_2$, produces quite high molar mass polymer, but with low regioregularity and capricious yield.

CONCLUSIONS

In conclusion, we report a new zerovalent palladium complex with tri(2-thienyl)phosphine as ligands; X-ray crystallography and computational chemistry are used to reveal its exact structure; for the first time, this complex has been used as catalyst precursor for the coupling of thiophene-based substrates. Our work clearly demonstrates that Pd(PTh$_3$)$_3$ is superior to Pd(PPh$_3$)$_4$, in catalyzing Suzuki-Miyaura coupling and polymerization of thiophene-based substrates. The combination of Pd(PTh$_3$)$_3$ and monomer 3 afforded high-molecular-weight P3HT with high regularity. Ongoing studies are directed at the reaction and the development of novel 2-thienylphosphine-based ligands for Suzuki polycondensation of thiophene-based bromo monomers.

**Scheme 1.** Synthesis of P3HT by SPC with Pd(PPh$_3$)$_4$ or Pd(PTh$_3$)$_3$ as catalyst precursors.

**Table 2.** $M_w$, $M_w/M_n$, and Yields of SPC of Monomers 3 and 4 Under Different Conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomer</th>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>3</td>
<td>Pd(PTh$_3$)$_3$</td>
<td>72</td>
<td>26,000</td>
<td>2.29</td>
</tr>
<tr>
<td>2b</td>
<td>3</td>
<td>Pd(PTh$_3$)$_3$</td>
<td>68</td>
<td>15,500</td>
<td>1.57</td>
</tr>
<tr>
<td>3c</td>
<td>3</td>
<td>Pd(PTh$_3$)$_3$</td>
<td>62</td>
<td>14,800</td>
<td>1.47</td>
</tr>
<tr>
<td>4a</td>
<td>4</td>
<td>Pd(PTh$_3$)$_3$</td>
<td>20</td>
<td>7,800</td>
<td>1.21</td>
</tr>
<tr>
<td>5b</td>
<td>4</td>
<td>Pd(PTh$_3$)$_3$</td>
<td>30</td>
<td>11,300</td>
<td>1.33</td>
</tr>
<tr>
<td>6c</td>
<td>4</td>
<td>Pd(PTh$_3$)$_3$</td>
<td>27</td>
<td>11,400</td>
<td>1.32</td>
</tr>
<tr>
<td>7a</td>
<td>3</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>22</td>
<td>13,900</td>
<td>1.61</td>
</tr>
<tr>
<td>8a</td>
<td>4</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>11</td>
<td>4,800</td>
<td>1.17</td>
</tr>
</tbody>
</table>

* THF/H$_2$O.
* THF/toluene/H$_2$O = 4/4/1.
* THF/toluene/H$_2$O = 4/1/1.

* Determined by GPC with polystyrene standards (Eluent: THF).

**Chart 1.** The chemical structures of Buchwald-type ligands.
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REFERENCES AND NOTES