

Communication

# Intramolecular Transfer of Pd Catalyst on Carbon–Carbon Triple Bond and Nitrogen–Nitrogen Double Bond in Suzuki–Miyaura Coupling Reaction

Takeru Kamigawara, Hajime Sugita, Koichiro Mikami, Yoshihiro Ohta and Tsutomu Yokozawa \*

Department of Materials and Life Chemistry, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan; katze102@icloud.com (T.K.); h.sugita1992@gmail.com (H.S.); koichiro.mikami@sagami.or.jp (K.M.); y-ohta0112@kanagawa-u.ac.jp (Y.O.)

\* Correspondence: yokozt01@kanagawa-u.ac.jp; Tel.: +81-45-481-5661

Academic Editor: Ioannis D. Kostas

Received: 24 March 2017; Accepted: 20 June 2017; Published: 23 June 2017

**Abstract:** Intramolecular transfer of *t*-Bu<sub>3</sub>P-ligated Pd catalyst on a carbon–carbon triple bond (C≡C) and nitrogen–nitrogen double bond (N=N) was investigated and compared with the case of a carbon–carbon double bond (C=C), which is resistant to intramolecular transfer of the Pd catalyst. Suzuki–Miyaura coupling reaction of equimolar 4,4′-dibromotolan (**1a**) or 4,4′-dibromoazobenzene (**1b**) with 3-isobutoxyphenylboronic acid (**2**) was carried out in the presence of *t*-Bu<sub>3</sub>P-ligated Pd precatalyst **3** and KOH/18-crown-6 as a base at room temperature. In both cases, the diphenyl-substituted product was selectively obtained, indicating that the Pd catalyst walked from one benzene ring to the other through the C≡C or N=N bond after the first substitution with **2**. Taking advantage of this finding, we conducted unstoichiometric Suzuki–Miyaura polycondensation of 1.3 equiv. of **1** and 1.0 equiv. of phenylenediboronic acid (ester) **6** in the presence of **3** and CsF/18-crown-6 as a base, obtaining high-molecular-weight conjugated polymer with a boronic acid (ester) moiety at both ends, contrary to the Flory principle.

**Keywords:** palladium catalyst; Suzuki coupling; catalyst transfer; conjugated polymer; unstoichiometric polycondensation

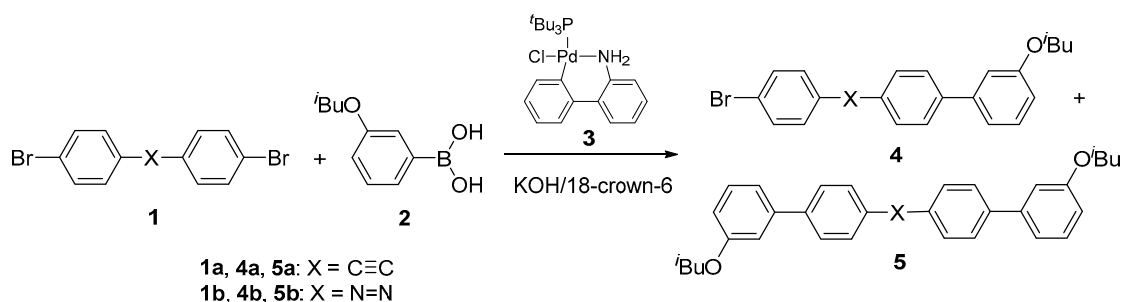
## 1. Introduction

Suzuki–Miyaura coupling reaction is a powerful protocol for the synthesis of polyarylenes containing  $\pi$ -conjugated polymers [1]. We have found that *t*-Bu<sub>3</sub>PPd(Ar)Br [2,3] initiates chain-growth Suzuki–Miyaura coupling polymerization of haloarylboronic acid (ester) as an AB type monomer to afford well-defined polyfluorene [4], poly(*p*-phenylene) [5], and poly(hexylthiophene) [6], and other researchers have obtained well-defined poly(phenanthrene) [7] and poly(fluorene-*alt*-benzothiadiazole) [8]. The chain-growth polymerization progresses via intramolecular transfer of the Pd catalyst to the terminal C–X (X = halogen) bond after reductive elimination of polymer–Pd–ArX. Therefore, these types of chain-growth polymerizations, including Kumada–Tamao and other coupling polymerizations, are known as catalyst-transfer condensation polymerizations (CTCPs) [9,10].

When this *t*-Bu<sub>3</sub>PPd(0) catalyst, which has a propensity for intramolecular catalyst transfer on a  $\pi$ -electron face, was used for Suzuki–Miyaura coupling polymerization of dibromoarene and arenyldiboronic acid ester (AA + BB polycondensation), high-molecular-weight  $\pi$ -conjugated polymer with a boronate moiety at both ends was obtained, even though excess dibromoarene was used [11]. This unstoichiometric polycondensation behavior is accounted for by successive substitution of the bromides in dibromoarene with arenyldiboronic acid ester or oligomers having boronate moieties at

both ends through intramolecular transfer of the Pd catalyst on the  $\pi$  face of dibromoarene. However, Suzuki–Miyaura coupling reaction of 4,4'-dibromostilbene with phenylboronic acid in the presence of  $t\text{-Bu}_3\text{PPd}(0)$  catalyst did not selectively afford diphenyl-substituted stilbene, implying that the Pd catalyst did not walk from one benzene ring to the other through the carbon–carbon double bond ( $\text{C}=\text{C}$ ) in the stilbene after the first substitution of 4,4'-dibromostilbene with phenylboronic acid [12]. We found that this failure of intramolecular catalyst transfer is due to bimolecular intermolecular transfer of  $t\text{-Bu}_3\text{PPd}(0)$  on the  $\text{C}=\text{C}$  of dibromostilbene to the  $\text{C}=\text{C}$  of another dibromostilbene. However, this intermolecular transfer of the catalyst could be suppressed by introduction of alkoxy groups at the ortho positions of the  $\text{C}=\text{C}$ .

We were next interested in whether or not the Pd catalyst undergoes intramolecular catalyst transfer on other multiple bonds. In the present study, we investigated catalyst transfer on a carbon–carbon triple bond ( $\text{C}\equiv\text{C}$ ) and nitrogen–nitrogen double bond ( $\text{N}=\text{N}$ ) by means of Suzuki–Miyaura coupling reaction of 4,4'-dibromotolan (**1a**) or 4,4'-dibromoazobenzene (**1b**) with phenylboronic acid **2** in the presence of  $t\text{-Bu}_3\text{PPd}(0)$  precatalyst **3** [13] (Scheme 1). If the catalyst undergoes intramolecular transfer on the multiple bond X in **1** and then inserts itself into the  $\text{C}-\text{Br}$  bond after the first substitution, the main product would be disubstituted **5**. On the other hand, if the catalyst diffuses into the reaction mixture after the first substitution, the main product would be monosubstituted **4**. Bielawski and coworkers have demonstrated intramolecular catalyst transfer of  $t\text{-Bu}_3\text{PPd}(0)$  catalyst on  $\text{C}\equiv\text{C}$  in Stille CTCP of 4-(tributylstannylethynyl)-2,5-dialkoxyiodobenzene as an AB monomer [14]. However, this catalyst transfer on  $\text{C}\equiv\text{C}$  might be dependent on the steric effect of the tributylstannyl and/or alkoxy groups, as in the case of catalyst transfer on  $\text{C}=\text{C}$  in *o*-alkoxy-substituted stilbene. In the present work, we found that  $t\text{-Bu}_3\text{PPd}(0)$  catalyst undergoes intramolecular catalyst transfer on  $\text{C}\equiv\text{C}$  and  $\text{N}=\text{N}$  even if the benzene rings adjacent to these multiple bonds are unsubstituted, in contrast to the case of catalyst transfer on  $\text{C}=\text{C}$ . To demonstrate effective catalyst transfer on  $\text{C}\equiv\text{C}$  and  $\text{N}=\text{N}$ , we further conducted unstoichiometric Suzuki–Miyaura polycondensation of excess **1** and 1.0 equiv. of phenylenediboronic acid (ester) in the presence of **3**, obtaining  $\pi$ -conjugated polymer with a boronate moiety at both ends.



**Scheme 1.** Suzuki–Miyaura coupling reaction of **1** with **2** in the presence of **3** to examine intramolecular catalyst transfer on the multiple bond X in **1**.

## 2. Results and Discussion

### 2.1. Suzuki–Miyaura Coupling Reaction of **1** with **2**

Intramolecular catalyst transfer on  $\text{C}\equiv\text{C}$  was first investigated by Suzuki–Miyaura coupling reaction of equimolar **1a** with **2** in the presence of 5 mol % of  $t\text{-Bu}_3\text{PPd}(0)$  precatalyst **3** and KOH/18-crown-6 (Table 1). In order to determine the product ratio of monosubstituted **4a** to disubstituted **5a** by means of gas chromatography (GC), authentic **4a** and **5a** were prepared by the reaction of equimolar **1a** and **2** in the presence of  $(\text{Ph}_3\text{P})_4\text{Pd}$ , which has no propensity for intramolecular catalyst transfer on a  $\pi$  face, and by the reaction of **1a** and 2 equiv. of **2** in the presence of **3**, respectively.

**Table 1.** Suzuki–Miyaura coupling reaction of **1** with **2** in the presence of **3** <sup>1</sup>.

Entry	1	Additive	Conv. of 1 (%) <sup>2</sup>	Yield of 4 and 5 (%) <sup>2</sup>	4:5 <sup>2</sup>
1	<b>1a</b>	-	74	70	6:94
2	<b>1a</b>	styrene	80	77	74:26
3	<b>1a</b>	stilbene	74	66	23:77
4	<b>1a</b>	phenylacetylene	97	56	35:65
5	<b>1a</b>	tolan	69	66	8:92
6	<b>1a</b>	1-phenyl-1-propyne	67	62	10:90
7 <sup>3</sup>	<b>1b</b>	-	61 <sup>4</sup>	52 <sup>4</sup>	11:89 <sup>4</sup>

<sup>1</sup> Reaction of **1** and **2** was carried out in the presence of 5.0 mol % of **3**, KOH (4.5 equiv.)/18-crown-6 (8.0 equiv.), and 4 equiv. of additive in THF ( $[1]_0 = 1.60 \times 10^{-2}$  M) and water (THF/water = 26.7/1, v/v) at rt for 2 h; <sup>2</sup> Determined by GC; <sup>3</sup> Reaction was carried out for 24 h; <sup>4</sup> Determined from the <sup>1</sup>H NMR spectra.

In the reaction of **1a** with **2**, disubstituted **5a** was obtained with high selectivity (Entry 1). Furthermore, the product ratio of **5a** was consistently more than 90% from the beginning of the reaction (Figure S1). This is important, because if **5a** was selectively formed due to higher reactivity of **4a** than **1a**—i.e., not via the catalyst-transfer mechanism—then **4a** should be accumulated at the beginning of the reaction, in which the concentration of **1a** is much higher than that of **4a** [15]. Therefore, these results indicate that intramolecular transfer of *t*-Bu<sub>3</sub>PPd(0) catalyst on C≡C took place, in contrast to the case of the reaction of 4,4'-dibromostilbene with **2** in the presence of *t*-Bu<sub>3</sub>PPd(0) catalyst, which afforded mainly monosubstituted stilbene [12]. We next examined the effects of additives to see whether intramolecular catalyst transfer on C≡C is disturbed by additives containing C=C or C≡C. If the affinity of an additive for *t*-Bu<sub>3</sub>PPd(0) is stronger than that of C≡C, the additive would trap the Pd catalyst during intramolecular catalyst transfer on **1a**, resulting in a decrease of the ratio of disubstituted **5a**. In the case of styrene as an additive, the ratio of **5a** was drastically decreased to 26% (Entry 2), whereas stilbene resulted in decrease to 77% (Entry 3). It turned out that terminal C=C disturbed intramolecular catalyst transfer on C≡C more strongly than did internal C=C. As for additives containing C≡C, phenylacetylene also induced a decrease of the ratio of **5a** (entry 4), whereas tolan and 1-phenyl-1-propyne did not affect the intramolecular transfer of the catalyst, and **5a** was selectively formed (Entries 5 and 6). Consequently, compounds bearing internal C≡C, including substrate **1a**, turned out not to disturb intramolecular catalyst transfer on C≡C.

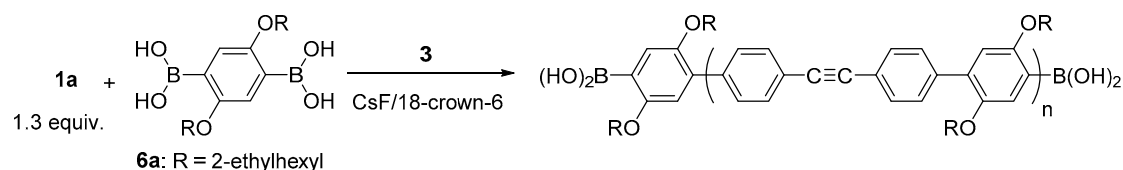
We next investigated intramolecular catalyst transfer on N=N. Suzuki–Miyaura coupling reaction of 4,4'-dibromoazobenzene (**1b**) with **2** was similarly carried out. Products **4b** and **5b** were isolated by preparative HPLC, and we confirmed that aromatic proton signals of **1b**, **4b**, and **5b** appeared separately in <sup>1</sup>H NMR spectra (Figure S2). The same reaction was conducted again in the presence of 1,4-bis(hexyloxy)benzene as an internal standard, and conversion of **1b** and the product ratio of **4b** to **5b** were determined by <sup>1</sup>H NMR spectroscopy. The ratio of **4b** to **5b** was 11:89, indicating that intramolecular catalyst transfer also took place on N=N (Entry 7), although the ratio of **5b** was slightly decreased as compared to the case of reaction of **1a** with **2** (Entry 1).

The observation that *t*-Bu<sub>3</sub>PPd(0) catalyst underwent intramolecular catalyst transfer on C≡C and N=N, in contrast to the case of C=C, might be accounted for by lower stability of the  $\eta^2$  coordination complexes of these multiple bonds to *t*-Bu<sub>3</sub>PPd, compared with the  $\eta^2$  complex of C=C. As the  $\eta^2$  complex becomes less stable, the chance of bimolecular ligand exchange of  $\eta^2$  complex between multiple bonds would be decreased. The observation that intramolecular catalyst transfer on C≡C is disturbed by additives containing C=C implies that the  $\eta^2$  complex of C=C is more stable than that of C≡C. In addition, density functional theory (DFT) calculations were performed to estimate the stability of the  $\eta^2$  coordination complexes of these multiple bonds with *t*-Bu<sub>3</sub>PPd. The values of stabilization energy of complexation of stilbene, tolan, and azobenzene with *t*-Bu<sub>3</sub>PPd were −27.9, −25.6, and −20.8 kcal/mol, respectively (Figures S3–S5). These results support our interpretation, although calculations for model PdPH<sub>3</sub> systems with ethylene and acetylene indicated that the Pd–C bonds are stronger in the acetylene complex than in the ethylene complex [16,17].

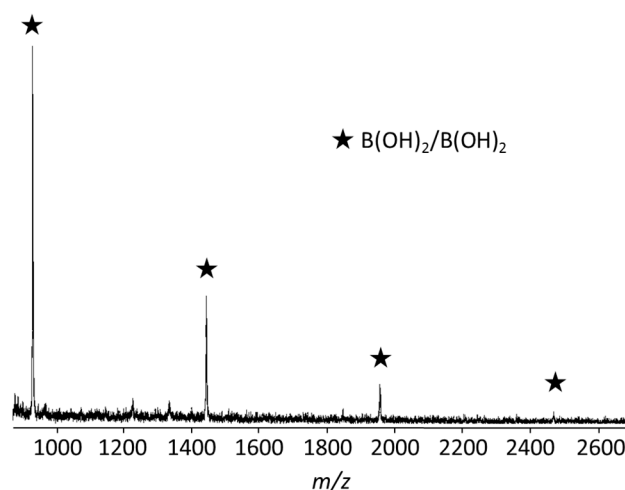
## 2.2. Unstoichiometric Suzuki–Miyaura Polycondensation

### 2.2.1. Polycondensation of Dibromotolan and Phenylenediboronic Acid (Ester)

Since we found that *t*-Bu<sub>3</sub>PPd(0) catalyst undergoes intramolecular catalyst transfer on C≡C, we conducted unstoichiometric Suzuki–Miyaura polycondensation of 1.3 equiv. of **1a** and 1.0 equiv. of phenylenediboronic acid **6a** in the presence of Pd catalyst **3** and CsF/18-crown-6 as a base at room temperature to afford polymer with *M<sub>n</sub>* of 5500 Da and *M<sub>w</sub>*/*M<sub>n</sub>* of 3.95 (Scheme 2). The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum of the polymer showed one series of peaks due to polymer with a boronic acid moiety at both ends (Figure 1). These results indicated that the polymerization involved intramolecular catalyst transfer on C≡C-containing monomer **1a**.



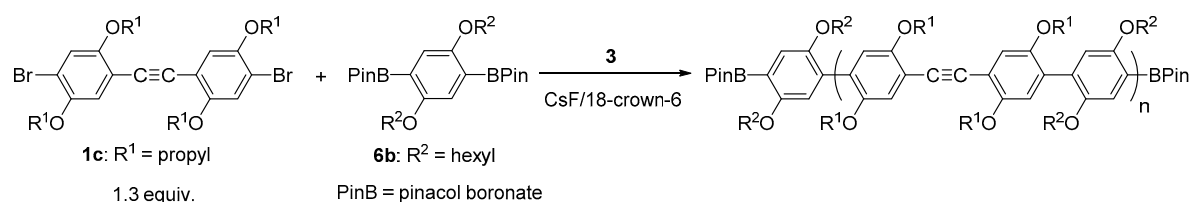
**Scheme 2.** Unstoichiometric Suzuki–Miyaura polycondensation of **1a** with **6a** in the presence of **3**.



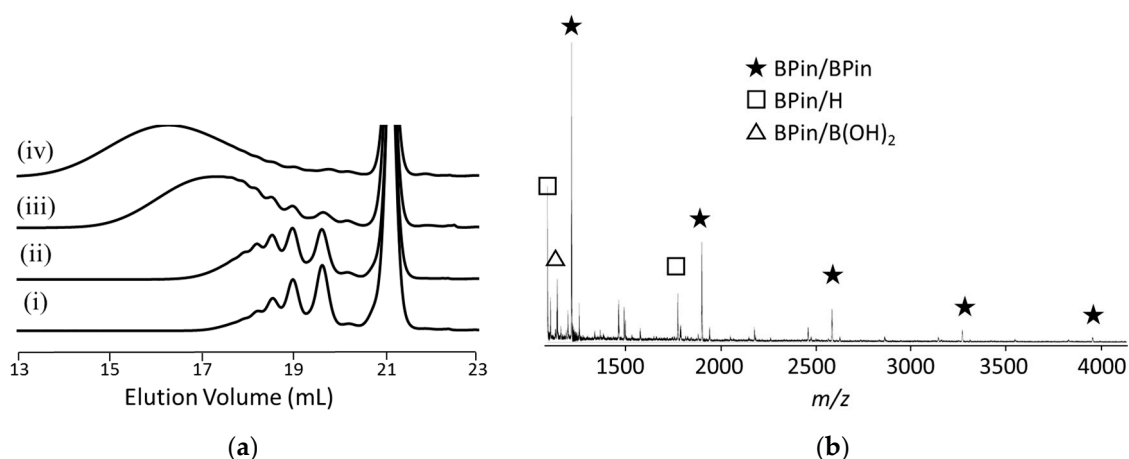
**Figure 1.** MALDI-TOF MS spectrum of polymer obtained by the polymerization of 1.3 equiv. of **1a** and 1.0 equiv. of **6a** in the presence of 2.0 mol % of **3**, CsF (5 equiv.), and 18-crown-6 (8 equiv.) in THF ([**6a**] =  $8.33 \times 10^{-3}$  M) and water (THF/water = 30/1, *v/v*) at rt for 15 h, followed by quenching with 1 M hydrochloric acid.

The polymerization of alkoxy-substituted dibromotolan **1c** and alkoxy-substituted phenylene diboronic acid ester **6b** was also conducted under similar conditions (Scheme 3). The molecular weight increased with reaction time and reached *M<sub>n</sub>* = 10,500 Da (*M<sub>w</sub>*/*M<sub>n</sub>* = 2.77) (Figure 2a), even though 1.3 equiv. of **1c** was used. The MALDI-TOF mass spectrum of polymer obtained at 24 h similarly showed major peaks due to polymer with a boronic acid ester moiety at both ends (BPin/BPin). Minor peaks in the lower-molecular-weight region are assignable to BPin/H and BPin/B(OH)<sub>2</sub>, which would be formed by hydrolysis of polymer–Pd–Br and the pinacol boronate moiety, respectively, by hydrochloric acid used to quench the polymerization. Formation of higher-molecular-weight polymer, in contrast to the polymerization of unsubstituted tolan **1a** with **6a**, is presumably accounted for by a higher propensity for intramolecular catalyst transfer on **1c** than **1a**, as in the case of Suzuki–Miyaura

coupling reaction of dibromostilbene with phenylboronic acid: alkoxy groups at the ortho position of C=C of stilbene promoted intramolecular catalyst transfer, as mentioned in the Introduction.



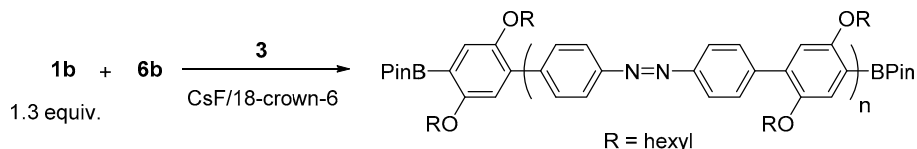
**Scheme 3.** Unstoichiometric Suzuki–Miyaura polycondensation of **1c** with **6b** in the presence of **3**.



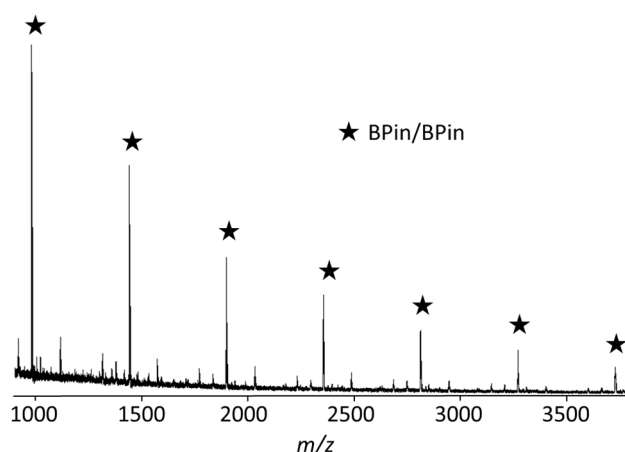
**Figure 2.** Unstoichiometric Suzuki–Miyaura polycondensation of 1.3 equiv. of **1c** with 1.0 equiv. of **6b** in the presence of 2.0 mol % of **3**, CsF (5.0 equiv.), and 18-crown-6 (8.0 equiv.) in THF ( $[\text{6b}] = 8.33 \times 10^{-3} \text{ M}$ ) and water (THF/water = 30/1,  $v/v$ ) at rt: (a) GPC profiles of polymer obtained at (i) 1 h ( $M_n = 2470 \text{ Da}$ ,  $M_w/M_n = 1.29$ ), (ii) 5 h ( $M_n = 3000 \text{ Da}$ ,  $M_w/M_n = 1.39$ ), (iii) 24 h ( $M_n = 6640 \text{ Da}$ ,  $M_w/M_n = 2.03$ ), (iv) 48 h ( $M_n = 10,500 \text{ Da}$ ,  $M_w/M_n = 2.77$ ); (b) MALDI-TOF mass spectra of polymer obtained at 24 h ( $M_n = 6640 \text{ Da}$ ,  $M_w/M_n = 2.03$ ).

## 2.2.2. Polycondensation of Dibromoazobenzene and Phenylenediboronic Acid Ester

We applied intramolecular catalyst transfer on N=N, as mentioned in Section 2.1, for unstoichiometric polycondensation of 1.3 equiv. of dibromoazobenzene **1b** and 1.0 equiv. of phenylenediboronic acid ester **6b** in the presence of Pd catalyst **3** (Scheme 4). The polymerization proceeded homogeneously, but polymer was precipitated at 42 h. Accordingly, the THF-soluble part of the polymer obtained at 42 h was analyzed. The GPC elution curve of the obtained polymer showed  $M_n = 5500 \text{ Da}$  and  $M_w/M_n = 1.44$ , and the polymer ends were confirmed to be BPin/BPin by MALDI-TOF mass spectrometry (Figure 3). Therefore, it turned out that polycondensation involving intramolecular catalyst transfer on **1b** proceeded, although high-molecular-weight polymer was not obtained due to the low solubility of the polymer in THF.



**Scheme 4.** Unstoichiometric Suzuki–Miyaura polycondensation of **1b** with **6b** in the presence of **3**.



**Figure 3.** MALDI-TOF MS spectrum of polymer obtained by the polymerization of 1.3 equiv. of **1b** and 1.0 equiv. of **6b** in the presence of 2.0 mol % of **3**, CsF (5 equiv.), and 18-crown-6 (8 equiv.) in THF ( $[\mathbf{6b}] = 8.33 \times 10^{-3}$  M) and water (THF/water = 30/1, *v/v*) at rt for 42 h, followed by quenching with 1 M hydrochloric acid.

In order to obtain more soluble polymer, polymerization of **1b** with **6a**, bearing a 2-ethylhexyloxy group, was carried out. The polymerization proceeded homogeneously, and the molecular weight was increased to 8300. However, the molecular weight distribution was exceptionally broad ( $M_w/M_n = 12.4$ ); the reason for this is not clear at present. Probably due to this broad molecular weight distribution, the MALDI-TOF mass spectrum did not show clear peaks in the region of molecular weight higher than 2000 Da.

### 3. Materials and Methods

#### 3.1. Materials

All starting materials were purchased from commercial suppliers (TCI, Aldrich, Wako, and Kanto, Tokyo, Japan) and used without further purification. Dry tetrahydrofuran (THF, stabilizer-free, Kanto, Tokyo, Japan) and distilled water (Wako, Tokyo, Japan) were used as received. Dibromoazobenzene **1b** [18] and phenylenediboronic acid **6a** [11] were prepared according to the literature.

#### 3.2. Measurements

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on JEOL ECA-500 (JEOL, Tokyo, Japan) and ECA-600 spectrometers (JEOL, Tokyo, Japan). The internal standard for  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  was tetramethylsilane (0.00 ppm) and the internal standard for  $^{13}\text{C}$  NMR spectra in  $\text{CDCl}_3$  was the midpoint of  $\text{CDCl}_3$  (77.0 ppm). IR spectra were recorded on a JASCO FT/IR-410 (JASCO, Tokyo, Japan). All melting points were measured with a Yanagimoto hot stage melting point apparatus (Yanaco, Tokyo, Japan) without correction. GC was performed on a Shimadzu GC-14B gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a Shimadzu fused silica capillary column CBP1-W12-100 (12 m length, 0.53 mm i.d.) and a flame ionization detector (FID). Isolation of **4b** and **5b** was carried out on a Japan Analytical Industry LC908-C60 recycling preparative HPLC (eluent,  $\text{CHCl}_3$ ) (JAI, Tokyo, Japan) with two JAIGEL columns (1H-40 and 2H-40). Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck, Darmstadt, Germany) with a specified solvent. The  $M_n$  and  $M_w/M_n$  values of polymer were measured on a Tosoh HLC-8020 gel permeation chromatography (GPC) unit (eluent, THF; calibration, polystyrene standards) (Tosoh, Yamaguchi, Japan) with two TSK-gel columns ( $2 \times$  Multipore  $\text{H}_{\text{XL}}\text{-M}$ ). MALDI-TOF mass spectra were recorded on a Shimadzu/Kratos AXIMA-CFR plus (Shimadzu, Kyoto, Japan) in the reflectron ion mode.



(laser  $\lambda$  = 337 nm). DCTB (trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as the matrix for the MALDI-TOF mass measurements.

### 3.3. Synthesis of Monosubstituted Tolan 4a

Transfer of reagents and withdrawal of small aliquots of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. A two-necked round-bottomed flask was equipped with a three-way stopcock and a dimroth condenser. Dibromotolan **1a** (134.9 mg, 0.40 mmol), phenylboronic acid **2** (81.4 mg, 0.42 mmol),  $(PPh_3)_4Pd$  (23.3 mg, 0.020 mmol),  $K_3PO_4$  (370.9 mg, 1.75 mmol), and 18-crown-6 (846 mg, 3.26 mmol) were placed in the flask, and the flask was flushed with argon. Dry THF (10.0 mL) and distilled water (0.60 mL) were added to the flask via a syringe, and the reaction mixture was refluxed for 3 h. The reaction was quenched with 1 M hydrochloric acid, and the mixture was extracted with  $CHCl_3$ . The organic layer was washed with water and dried over anhydrous  $MgSO_4$ . The solvent was removed under reduced pressure, and the residue was purified by means of column chromatography ( $SiO_2$ , hexane) to afford **4a** as a pale yellow viscous liquid (111.3 mg, 69%); mp 96–99 °C.

$^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.58 (s, 4H), 7.50 (d,  $J$  = 8.6 Hz, 2H), 7.40 (d,  $J$  = 8.6 Hz, 2H), 7.35 (t,  $J$  = 8.0 Hz, 1H), 7.18 (d,  $J$  = 6.9 Hz, 1H), 7.13 (s, 1H), 6.90 (dd,  $J$  = 5.7 Hz and 2.3 Hz, 1H), 3.78 (d,  $J$  = 6.9 Hz, 2H), 2.14–2.10 (m, 1H), 1.05 (d,  $J$  = 6.3 Hz, 6H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  159.7, 141.8, 140.9, 132.0, 129.8, 127.3, 122.3, 119.3, 113.4, 90.0, 75.6, 30.9, 28.3, 19.3; IR (KBr) 3460, 2908, 1606, 1471, 1350, 1206, 1105, 965, 776, 690, 513  $cm^{-1}$ .

### 3.4. Synthesis of Disubstituted Tolan 5a

Transfer of reagents and withdrawal of small aliquots of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. Dibromotolan **1a** (134.3 mg, 0.40 mmol), **2** (157.7 mg, 0.81 mmol), **3** (10.2 mg, 0.020 mmol), KOH (105.4 mg, 1.88 mmol), and 18-crown-6 (861.0 mg, 3.26 mmol) were placed in a flask equipped with a three-way stop cock, and the atmosphere in the flask was replaced with argon. Dry THF (10.0 mL) and distilled water (0.60 mL) were added to the flask via a syringe, and the mixture was degassed under reduced pressure and filled with argon. The reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with hydrochloric acid, and the mixture was extracted with  $CHCl_3$ . The organic layer was washed with water and dried over anhydrous  $MgSO_4$ . The solvent was removed under reduced pressure, and the residue was purified by means of column chromatography ( $SiO_2$ , hexane) to afford **5a** as a dark yellow viscous solid (184.1 mg, 96%); mp 130–134 °C.

$^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.60 (s, 8H), 7.35 (t,  $J$  = 7.7 Hz, 2H), 7.18 (d,  $J$  = 7.7 Hz, 2H), 7.15 (s, 2H), 6.90 (dd,  $J$  = 6.0 and 2.0 Hz, 2H), 3.79 (d,  $J$  = 6.6 Hz, 4H), 2.13–2.10 (m, 2H), 1.04 (d,  $J$  = 6.9 Hz, 12H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  167.7, 152.2, 147.2, 144.7, 130.8, 124.5, 115.5, 114.2, 83.9, 69.8, 29.7, 24.8; IR (KBr) 3461, 2907, 1606, 1522, 1295, 1206, 1050, 1013, 873, 830, 776, 690, 538  $cm^{-1}$ .

### 3.5. Synthesis of Mono- and Disubstituted Azobenzene 4b and 5b

Transfer of reagents and withdrawal of small aliquots of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. Dibromoazobenzene **1b** (50.9 mg, 0.15 mmol), **2** (30.6 mg, 0.16 mmol), **3** (4.2 mg, 0.016 mmol), KOH (37.8 mg, 0.68 mmol), and 18-crown-6 (318.4 mg, 1.2 mmol) were placed in a flask equipped with a three-way stop cock, and the atmosphere in the flask was replaced with argon. Dry THF (6.0 mL) and distilled water (0.36 mL) were added to the flask via a syringe, and the mixture was degassed under reduced pressure and filled with argon. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with hydrochloric acid, and the mixture was extracted with  $CHCl_3$ . The organic layer was washed with water and dried over anhydrous  $MgSO_4$ . The solvent was removed under reduced pressure, and the residue was purified by means of HPLC to afford **4b** as a pale yellow viscous solid (10.4 mg, 17%) and **5b** as a pale yellow viscous solid (22.3 mg, 31%).

**4b**: mp 89–95 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 8.6 Hz, 2H), 7.82 (d,  $J$  = 8.9 Hz, 2H), 7.74 (d,  $J$  = 8.6 Hz, 2H), 7.66 (d,  $J$  = 8.6 Hz, 2H), 7.37 (t,  $J$  = 8.0 Hz, 1H), 7.24 (d,  $J$  = 7.7 Hz, 1H), 7.20 (s, 1H), 6.94 (dd,  $J$  = 7.7 and 1.7 Hz, 1H), 3.80 (d,  $J$  = 6.6 Hz, 1H), 2.16–2.10 (m, 1H), 1.06 (d,  $J$  = 6.6 Hz, 6H),  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 151.9, 143.6, 141.6, 129.8, 127.8, 123.3, 119.4, 113.8, 113.6, 74.5, 28.3, 19.3, IR (KBr) 3460, 2911, 1599, 1469, 1397, 1217, 1108, 965, 840, 610, 552  $\text{cm}^{-1}$ .

**5b**: mp 195–198 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J$  = 8.6 Hz, 4H), 7.75 (d,  $J$  = 8.3 Hz, 4H), 7.37 (t,  $J$  = 8.0 Hz, 2H), 7.24 (d,  $J$  = 8.3 Hz, 2H), 7.20 (s, 2H), 6.93 (dd,  $J$  = 6.3 and 2.0 Hz, 2H), 3.81 (d,  $J$  = 6.3 Hz, 4H), 2.17–2.11 (m, 2H), 1.06 (d,  $J$  = 6.6 Hz, 12H),  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 151.6, 132.3, 129.9, 128.3, 127.8, 124.3, 119.4, 113.9, 113.6, 77.3, 28.3, 19.3, IR (KBr) 3448, 2924, 2362, 1719, 1571, 1473, 1281, 1065, 1006, 835, 657, 577  $\text{cm}^{-1}$ .

### 3.6. Suzuki–Miyaura Coupling Reaction of **1a** with **2**

Transfer of reagents and withdrawal of small aliquots of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. Dibromotolan **1a** (0.100 mmol), **2** (0.105 mmol), **3** (0.005 mmol), KOH (0.5 mmol), 18-crown-6 (0.80 mmol), and 1,4-bis(hexyloxy)benzene (0.040 mmol) as an internal standard substance were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (4.0 mL), distilled water (0.40 mL), and additive (none or 0.100 mmol) were added to the flask via a syringe, and the mixture was degassed under reduced pressure and filled with argon. The reaction mixture was stirred at room temperature for 2 h, and the reaction was quenched with 1 M hydrochloric acid. The mixture was extracted with  $\text{CHCl}_3$ , and the organic layer was subjected to GC analysis for estimation of conversion of **1a** and the product ratio of **4a** to **5a**.

### 3.7. Suzuki–Miyaura Coupling Reaction of **1b** with **2**

Transfer of reagents and withdrawal of small aliquots of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. Dibromoazobenzene **1b** (50.9 mg, 0.15 mmol), **2** (30.6 mg, 0.16 mmol), **3** (4.2 mg, 0.008 mmol), KOH (37.8 mg, 0.68 mmol), 18-crown-6 (318.4 mg, 1.2 mmol), and 1,4-bis(hexyloxy)benzene (27.2 mg, 0.016 mmol) as an internal standard substance were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (6.0 mL) and distilled water (0.36 mL) were added to the flask via a syringe, and the mixture was degassed under reduced pressure and filled with argon. The reaction mixture was stirred at room temperature for 24 h, and the reaction was quenched with 1 M hydrochloric acid. The mixture was extracted with  $\text{CHCl}_3$  and dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The whole mixture was dissolved in  $\text{CDCl}_3$  and then subjected to  $^1\text{H}$  NMR analysis to determine conversion of **1b** and the product ratio of **4b** to **5b**.

### 3.8. Polycondensation of **1c** and **6b**

Transfer of reagents and withdrawal of small aliquots of the reaction mixture for analysis was carried out via a syringe from a three-way stopcock under a stream of nitrogen. Dibromo monomer **1c** (36.89 mg, 0.065 mmol), phenylenediboronic acid pinacol ester **6b** (26.91 mg, 0.051 mmol), CsF (34.1 mg, 0.22 mmol), 18-crown-6 (119.1 mg, 0.45 mmol), and **3** (1.4 mg, 0.027 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (6.0 mL) and distilled water (0.2 mL) were added to the flask via a syringe, and the mixture was degassed under reduced pressure and filled with argon. The reaction mixture was stirred at room temperature for two days, and the reaction was quenched with 1 M hydrochloric acid. The mixture was extracted with  $\text{CHCl}_3$ , and the organic layer was washed with water, then dried over anhydrous  $\text{MgSO}_4$ . Concentration under reduced pressure gave residue, which was purified by preparative HPLC to give polymer (32.7 mg, 94%).



#### 4. Conclusions

We have demonstrated that *t*-Bu<sub>3</sub>PPd(0) catalyst undergoes intramolecular transfer on C≡C and N=N, in contrast to the case of C=C, by means of Suzuki–Miyaura coupling reaction of equimolar dibromotolan **1a** or dibromoazobenzene **1b** with phenylboronic acid **2** in the presence of *t*-Bu<sub>3</sub>P-ligated Pd precatalyst **3** and by unstoichiometric polycondensation of **1** and phenyleneboronic acid (ester) **6** with **3**. In the former reaction, successive disubstitution of **1** with **2** selectively proceeded, and the latter polycondensation yielded high-molecular-weight conjugated polymer with a boronic acid (ester) moiety at both ends, even if excess dibromo monomer **1** was used. We believe these findings provide useful information about the requirements for Pd catalyst transfer on  $\pi$ -conjugated faces, as well as affording entry into a new class of  $\pi$ -conjugated polymer architectures via functionalization of chain-end boronate moieties.

**Supplementary Materials:** The following details are available online at [www.mdpi.com/2073-4344/7/7/195/s1](http://www.mdpi.com/2073-4344/7/7/195/s1), Synthesis of mono- and disubstituted tolan **4a** and **5a**, Synthesis of mono- and disubstituted azobenzene **4b** and **5b**, The product ratio of **5a** to **4a** and **5a** as a function of conversion of **1a**, Estimation of product ratio of **4b** to **5b** by <sup>1</sup>H NMR spectra, and DFT calculations for complexation of diphenylacetylene, stilbene, and azobenene with PdP(*t*-Bu)<sub>3</sub>.

**Acknowledgments:** This study was supported by a Grant in Aid (No. 15H03819) for Scientific Research from the Japan Society for the Promotion of Science (JSPS) and by the MEXT-Supported Program for the Strategic Research Foundation at Private Universities (No. S1311032), 2013–2018.

**Author Contributions:** H.S. and T.Y. conceived and designed the experiments; T.K. performed the experiments; K.M. and T.Y. analyzed the data; Y.O. contributed reagents/materials/analysis tools; T.Y. wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Sakamoto, J.; Rehahn, M.; Wegner, G.; Schlüter, A.D. Suzuki polycondensation: Polyarylenes à la carte. *Macromol. Rapid Commun.* **2009**, *30*, 653–687. [CrossRef] [PubMed]
2. Stambuli, J.P.; Bühl, M.; Hartwig, J.F. Synthesis, characterization, and reactivity of monomeric, arylpalladium halide complexes with a hindered phosphine as the only dative ligand. *J. Am. Chem. Soc.* **2002**, *124*, 9346–9347. [CrossRef] [PubMed]
3. Stambuli, J.P.; Incarvito, C.D.; Buhl, M.; Hartwig, J.F. Synthesis, structure, theoretical studies, and ligand exchange reactions of monomeric, T-shaped arylpalladium(II) halide complexes with an additional, weak agostic interaction. *J. Am. Chem. Soc.* **2004**, *126*, 1184–1194. [CrossRef] [PubMed]
4. Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. Chain-growth polymerization for the synthesis of polyfluorene via Suzuki–Miyaura coupling reaction from an externally added initiator unit. *J. Am. Chem. Soc.* **2007**, *129*, 7236–7237. [CrossRef] [PubMed]
5. Yokozawa, T.; Kohno, H.; Ohta, Y.; Yokoyama, A. Catalyst-transfer Suzuki–Miyaura coupling polymerization for precision synthesis of poly(*p*-phenylene). *Macromolecules* **2010**, *43*, 7095–7100. [CrossRef]
6. Yokozawa, T.; Suzuki, R.; Nojima, M.; Ohta, Y.; Yokoyama, A. Precision synthesis of poly(3-hexylthiophene) from catalyst-transfer Suzuki–Miyaura coupling polymerization. *Macromol. Rapid Commun.* **2011**, *32*, 801–806. [CrossRef] [PubMed]
7. Verswyvel, M.; Hoebers, C.; De Winter, J.; Gerbaux, P.; Koeckelberghs, G. Study of the controlled chain-growth polymerization of poly(3,6-phenanthrene). *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 5067–5074. [CrossRef]
8. Elmaleh, E.; Kiriya, A.; Huck, W.T.S. Chain-growth Suzuki polymerization of n-type fluorene copolymers. *Macromolecules* **2011**, *44*, 9057–9061. [CrossRef]
9. Yokozawa, T.; Ohta, Y. Transformation of step-growth polymerization into living chain-growth polymerization. *Chem. Rev.* **2016**, *116*, 1950–1968. [CrossRef] [PubMed]
10. Yokozawa, T.; Ohta, Y. Chapter 1 controlled synthesis of conjugated polymers in catalyst-transfer condensation polymerization: Monomers and catalysts. In *Semiconducting Polymers: Controlled Synthesis and Microstructure*; The Royal Society of Chemistry: Cambridge, UK, 2017; pp. 1–37.

11. Nojima, M.; Kosaka, K.; Kato, M.; Ohta, Y.; Yokozawa, T. Alternating intramolecular and intermolecular catalyst-transfer Suzuki–Miyaura condensation polymerization: Synthesis of boronate-terminated  $\pi$ -conjugated polymers using excess dibromo monomers. *Macromol. Rapid Commun.* **2016**, *37*, 79–85. [[CrossRef](#)] [[PubMed](#)]
12. Nojima, M.; Ohta, Y.; Yokozawa, T. Structural requirements for palladium catalyst transfer on a carbon–carbon double bond. *J. Am. Chem. Soc.* **2015**, *137*, 5682–5685. [[CrossRef](#)] [[PubMed](#)]
13. Zhang, H.-H.; Xing, C.-H.; Tsemo, G.B.; Hu, Q.-S. *t*-Bu<sub>3</sub>P-coordinated 2-phenylaniline-based palladacycle complex as a precatalyst for the Suzuki cross-coupling polymerization of aryl dibromides with aryldiboronic acids. *ACS Macro Lett.* **2013**, *2*, 10–13. [[CrossRef](#)] [[PubMed](#)]
14. Kang, S.; Ono, R.J.; Bielawski, C.W. Controlled catalyst transfer polycondensation and surface-initiated polymerization of *p*-phenyleneethynylene-based monomer. *J. Am. Chem. Soc.* **2013**, *135*, 4984–4987. [[CrossRef](#)] [[PubMed](#)]
15. Bryan, Z.J.; Hall, A.O.; Zhao, C.T.; Chen, J.; McNeil, A.J. Limitations of using small molecules to identify catalyst-transfer polycondensation reactions. *ACS Macro Lett.* **2016**, *5*, 69–72. [[CrossRef](#)]
16. Zenkina, O.V.; Gidron, O.; Shimon, L.J.W.; Iron, M.A.; van der Boom, M.E. Mechanistic aspects of aryl–halide oxidative addition, coordination chemistry, and ring-walking by palladium. *Chem. Eur. J.* **2015**, *21*, 16113–16125. [[CrossRef](#)] [[PubMed](#)]
17. Zenkina, O.; Altman, M.; Leitun, G.; Shimon, L.J.W.; Cohen, R.; van der Boom, M.E. From azobenzene coordination to aryl–halide bond activation by platinum. *Organometallics* **2007**, *26*, 4528–4534. [[CrossRef](#)]
18. Ma, H.; Li, W.; Wang, J.; Xiao, G.; Gong, Y.; Qi, C.; Feng, Y.; Li, X.; Bao, Z.; Cao, W.; et al. Organocatalytic oxidative dehydrogenation of aromatic amines for the preparation of azobenzenes under mild conditions. *Tetrahedron* **2012**, *68*, 8358–8366. [[CrossRef](#)]



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).