

Structural Requirements for Palladium Catalyst Transfer on a Carbon–Carbon Double Bond

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S Supporting Information

ABSTRACT: Intramolecular transfer of $t\text{Bu}_3\text{PPd}(0)$ on a carbon–carbon double bond ($\text{C}=\text{C}$) was investigated by using Suzuki–Miyaura coupling reaction of dibromostilbenes with aryl boronic acid or boronic acid esters in the presence of various additives containing $\text{C}=\text{C}$ as a model. Substituent groups at the ortho position of $\text{C}=\text{C}$ of stilbenes are critical for selective intramolecular catalyst transfer and may serve to suppress formation of the bimolecular $\text{C}=\text{C}-\text{Pd}-\text{C}=\text{C}$ complex that leads to intermolecular transfer of $t\text{Bu}_3\text{PPd}(0)$.

π -Conjugated polymers have received much attention due to their potential applications in thin film transistors (TFTs),¹ organic light-emitting diodes (OLEDs),² and photovoltaic cells.³ Catalyst-transfer condensation polymerization (CTCP) is a powerful methodology for synthesis of well-defined π -conjugated polymers with controlled molecular weight and low polydispersity.⁴ We have proposed that this polymerization involves intramolecular catalyst transfer on the polymer backbone, and therefore a critical aspect of successful CTCP is selection of a catalyst with high activity and a high propensity for intramolecular catalyst transfer. In CTCP with palladium (Pd) catalysts, $t\text{Bu}_3\text{PPd}(\text{Ar})\text{Br}$ is widely used as a catalyst for the synthesis of a well-defined polyfluorene,⁵ polyphenylene,⁶ polythiophene,⁷ poly(flourene-*alt*-benzothiadiazole),⁸ and poly(*p*-phenyleneethynylene).⁹ We have attempted to utilize Suzuki–Miyaura¹⁰ and Mizoroki–Heck¹¹ CTCP with this Pd catalyst for synthesis of well-defined poly(phenylenevinylene) (PPV), which has been intensively investigated especially for application to OLEDs,^{2,12} in order to extend the range of CTCP for synthesis of not only aromatic conjugated polymers but also aromatic and carbon–carbon double bond ($\text{C}=\text{C}$) conjugated polymers. However, the molecular weight distribution of the obtained PPV was broad, and the aryl group of the $t\text{Bu}_3\text{PPd}(\text{Ar})\text{Br}$ catalyst was not introduced at the polymer end, indicating that $t\text{Bu}_3\text{PPd}(0)$ generated by the reaction of the Pd catalyst with the monomer underwent intermolecular transfer. These results imply that a $\text{C}=\text{C}$ bond in the monomer or in the polymer backbone may disturb intramolecular transfer of $t\text{Bu}_3\text{PPd}(0)$ during polymerization.

On the other hand, van der Boom and co-workers demonstrated that the reaction of $\text{Pt}(0)$ or $\text{Ni}(0)$ with a bromostilbene derivative resulted in selective $\eta^2\text{-C}=\text{C}$ coordination, which was kinetically preferred at low temperature, followed by intramolecular “ring walking” of the metal center and intramolecular oxidative addition of the aryl-bromide bond, which was

thermodynamically preferred when the temperature was raised.¹³ In accordance with this result, density functional theory calculation suggested that $\eta^2\text{-C}=\text{C}$ coordination is more stable than the free state.^{13b}

In the present study, we investigated why $t\text{Bu}_3\text{PPd}(0)$ did not undergo intramolecular transfer during polymerization of monomers containing $\text{C}=\text{C}$ by examining the Suzuki–Miyaura coupling reaction of dibromostilbene derivatives with aryl boronic acid or boronic acid esters in the presence and absence of additives containing $\text{C}=\text{C}$. We found that $t\text{Bu}_3\text{PPd}(0)$ on the π -face of the substrate readily undergoes intermolecular transfer to the $\text{C}=\text{C}$ of another substrate or additive molecule. Moreover, we found that this intermolecular transfer of the catalyst can be suppressed by introduction of alkoxy groups at the ortho positions of the $\text{C}=\text{C}$. To demonstrate the effectiveness of this strategy, we employed it to achieve selective disubstitution of α,ω -dibromo polystilbene with arylboronic acid ester via intramolecular transfer of $t\text{Bu}_3\text{PPd}(0)$ on the long conjugated backbone, which contains $\text{C}=\text{C}$.

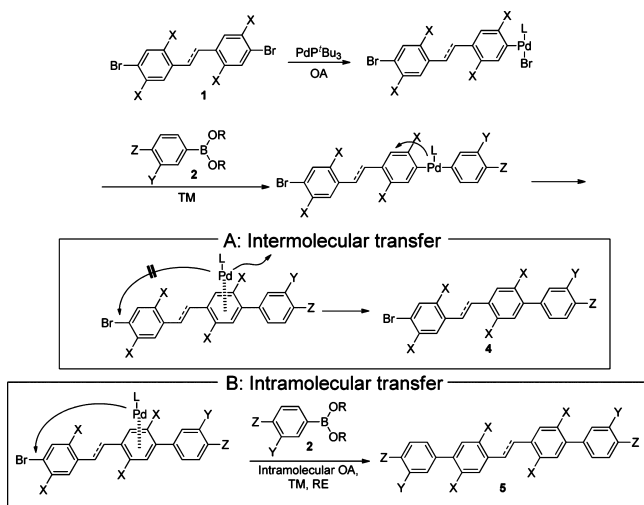
Suzuki–Miyaura coupling reaction of dibromostilbene **1** with equimolar arylboronic acid or boronic acid ester **2** was carried out in the presence of 5 mol % of $t\text{Bu}_3\text{PPd}(o\text{-tolyl})\text{Br}$ **3**,¹⁴ which generates $t\text{Bu}_3\text{PPd}(0)$ by reaction with **2**, to see whether or not the Pd catalyst undergoes intramolecular transfer (Scheme 1), in a similar manner to that employed by McCullough and co-workers to demonstrate intramolecular transfer of a Ni catalyst in Kumada–Tamao coupling reaction of 2,5-dibromothiophene with a Grignard reagent.¹⁵ In the reaction of **1** with **2**, the $\text{C}-\text{Br}$ bond of **1** first undergoes oxidative addition to $t\text{Bu}_3\text{PPd}(0)$, followed by transmetalation with **2** and reductive elimination to regenerate $t\text{Bu}_3\text{PPd}(0)$. If the $\text{Pd}(0)$ diffuses into the reaction mixture, the main product will be monosubstituted **4** (Scheme 1A). On the other hand, if the $\text{Pd}(0)$ inserts into the other $\text{C}-\text{Br}$ bond of **4** via intramolecular transfer, the main product will be disubstituted **5** (Scheme 1B). We determined the preferred behavior of PdP^tBu_3 by measuring the product ratio of **4** to **5**. To avoid issues with the solubility of products, an alkoxy side chain was introduced into **1** or **2**. Several derivatives **4** and **5** were separately prepared to aid in determining the ratio of **4** to **5** by means of ^1H NMR spectroscopy (see Supporting Information (SI)).

The reaction of *trans*-4,4'-dibromostilbene **1a** with *m*-isobutoxyphenylboronic acid **2a** was first carried out to afford **4** as a main product, implying that intramolecular transfer of $t\text{Bu}_3\text{PPd}(0)$ on $\text{C}=\text{C}$ did not take place (Table 1, entry 1).

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Scheme 1. Proposed Mechanisms for the Model Reaction Occurring through (A) Intermolecular and (B) Intramolecular Transfer of the Pd Catalyst



OA = oxidative addition, TM = transmetalation, RE = reductive elimination, L = P^tBu₃

1a: X = H, connector = C=C, 1b: X = OC₃H₇, connector = C=C, 1b': X = OC₃H₇, connector = C-C.

2a: Y = O^tBu, Z and R = H, 2b: Y and Z = H, R = pinacol ester,

2c: Y = H, Z = CH=CH₂, R = pinacol ester

Table 1. Model Reactions of 1 with 2

entry	1	2	additive	4:5 ^a
1	1a	2a	—	64:36
2	1b	2b	—	0:100
3	1b'	2b	—	42:58
4	1b	2c	—	66:33
5	1b	2b	styrene	60:40
6	1b	2b	stilbene	41:59
7	1b	2b	6	0:100

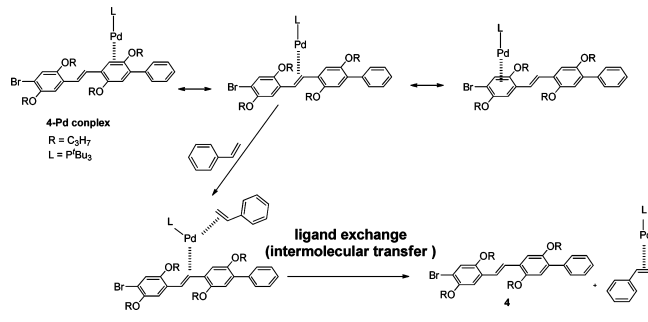
^aDetermined by ¹H NMR spectra.

However, the reaction of tetraalkoxy-substituted **1b** with phenylboronic acid ester **2b** exclusively yielded **5** (entry 2). A control experiment using diphenylethane derivative **1b'**, which was prepared by hydrogenation of the C=C of **1b**, afforded a mixture of mono- and disubstituted products (entry 3). This result strongly suggested that ^tBu₃PPd(0) walked from one benzene ring to the other benzene ring through C=C by virtue of coordination of the π-electrons of **1b**.

To investigate suitable conditions for polymerization of phenylenevinylene monomers, 4-vinylphenylboronic acid ester **2c** instead of **2b** was reacted with **1b**, resulting in a change of the major product to **4** (entry 4). Therefore, we considered that the alkoxy side chains of **1b** would play an important role in the intramolecular transfer of ^tBu₃PPd(0) through C=C, whereas ^tBu₃PPd(0) would diffuse into the reaction mixture from the C=C of unsubstituted **1a** or even the styryl **2c** unit in **4**, despite the alkoxy side chains. To test this hypothesis, reaction of **1b** with **2b** was carried out in the presence of styrene. In this case, the added styrene should not disturb intramolecular transfer of the Pd catalyst, which would afford **5** exclusively. However, in fact, the main product was **4** (entry 5), and thus it turned out that the added styrene acts as an inhibitor of intramolecular transfer of the Pd catalyst. This result indicated that intermolecular transfer of the catalyst takes place not by spontaneous diffusion of the catalyst into the reaction mixture, but by bimolecular ligand exchange reaction of the catalyst.

We propose that the intermolecular transfer of ^tBu₃PPd(0) might occur on the C=C of **4**. Thus, styrene would approach the η² coordination complex of the C=C of **4** to ^tBu₃PPd(0), which is the most stable coordination structure, and then the catalyst would move to the C=C of styrene (Scheme 2). This

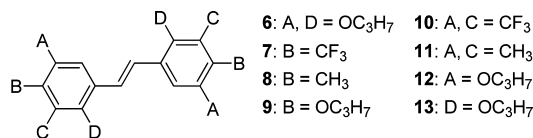
Scheme 2. Proposed Mechanism of Intermolecular Transfer of PdP^tBu₃



proposed mechanism is supported by the occurrence of selective disubstitution through intramolecular transfer of the catalyst on a dibromo substrate without C=C, 2,5-dibromothiophene, with **2b** even in the presence of styrene (see SI).

However, if all C=C compounds disturb intramolecular transfer of ^tBu₃PPd(0), **1b** would also have acted as an inhibitor. Thus, we examined the effects of stilbene and stilbene **6** (Chart 1) substituted with alkoxy side chains at the same

Chart 1. Chemical Structures of Additives 6–13



position as in **1b**, using the reaction of **1b** with **2b**. In the case of stilbene as an additive, **4** and **5** were formed (entry 6), whereas additive **6** did not affect the intramolecular transfer of the catalyst, and **5** was formed exclusively (entry 7). These results suggest that alkoxy side chains, which were introduced into dibromostilbene to increase solubility, also happened to promote intramolecular transfer of ^tBu₃PPd(0).

We next investigated what substituents at which positions on stilbene are necessary to avoid disturbance of the intramolecular transfer of the Pd catalyst in the reaction of **1b** and **2b**, using a variety of stilbenes as additives (Chart 1).

First, electrical substituent effects at the para position of stilbene were examined by the use of 7–9 (position B of Chart 1). In all cases, both **4** and **5** were formed, but the ratio of **4** was decreased in the order from an electron-withdrawing to electron-donating group (Table 2, entries 1–3), implying that the affinity of C=C of stilbene for ^tBu₃PPd(0) is presumably governed by back-donation from Pd(0) to the π* orbital of C=C,^{13c,16} probably because the LUMO level of stilbene is lower than that of aromatics. However, substituents at the meta position (positions A and C of Chart 1) did not influence the ratio of **4** to **5**: the same ratio was seen with both **10** (CF₃) and **11** (CH₃), and the selectivity for **5** was higher than that in the cases of *p*-substituted stilbenes (entries 4 and 5). Accordingly, intermolecular transfer of the catalyst to stilbene derivatives seems to be governed by the steric character

Table 2. Model Reactions of 1b with 2b in the Presence of Additives

entry	additive	A	B	C	D	4:5 ^a
1	7	H	CF ₃	H	H	55:45
2	8	H	CH ₃	H	H	31:69
3	9	H	OC ₃ H ₇	H	H	25:75
4	10	CF ₃	H	CF ₃	H	22:78
5	11	CH ₃	H	CH ₃	H	22:78
6	12	OC ₃ H ₇	H	H	H	32:67
7	13	H	H	H	OC ₃ H ₇	0:100

^aDetermined by ¹H NMR spectra.

around the C=C of stilbene, rather than the electronic effect of substituents.

We then examined the effect of the position of the alkoxy group of stilbene by using **9**, **12**, and **13**, which have a propoxy group at the para, meta, and ortho positions, respectively. *Para*- and *meta*-alkoxystilbene **9** and **12** resulted in formation of a mixture of **4** and **5** (entries 3 and 6), whereas the *ortho*-counterpart **13** gave exclusively **5** (entry 7). These results support the idea that alkoxy groups at the ortho position of C=C of stilbene suppress intermolecular transfer of ^tBu₃PPd(0). This behavior might be attributed to difficulty in the ligand exchange reaction of the η² coordination Pd complex of **4** with the C=C of stilbene **13** by virtue of steric hindrance of the alkoxy groups of **4** and **13** in the transition state (Scheme S2). Consequently, the failure of Suzuki–Miyaura CTCP of phenylenevinylene monomers¹⁰ is probably accounted for by insufficient steric bulkiness around the C=C of the monomers.

Since we had established the structural requirement for intramolecular transfer of ^tBu₃PPd(0) on the C=C, we next examined intramolecular transfer on longer conjugated systems containing C=C. First, the same reaction was carried out with alkoxy-substituted oligophenylenevinylene dibromide **S3** having two C=C; this afforded the corresponding disubstituted compound **S5** exclusively (Scheme S3). We next examined intramolecular transfer of ^tBu₃PPd(0) on a π-conjugated polymer with multiple C=C. For this purpose, α,ω-dibromo polystilbene was prepared by means of A₂ + B₂ type Suzuki–Miyaura polycondensation of dibromo monomer **1b** and the corresponding diboronic acid ester monomer having alkoxy side chains at the same position as in **1b**.

The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum of the obtained polystilbene showed that it contained mainly bromines at both ends (designated as Br/Br) (Figure 1a and SI). The number-average molecular weight (M_n) was estimated to be 4000 by means of gel permeation chromatography (GPC). The reaction of α,ω-dibromo polystilbene with equimolar tolylboronic acid ester **14**, the amount of which was roughly determined based on the M_n value of polystilbene, was carried out in the presence of 10 mol % of P(^tBu)₃PdG2, which generates ^tBu₃PPd(0) with a base,¹⁷ and CsF/18-crown-6 for 7.5 h (Scheme 3). The MALDI-TOF mass spectrum of the products contained two major series of polystilbene molecules with Br/Br and Tolyl/Tolyl ends, as well as a minor series of Tolyl/Br peaks (Figure 1b). Therefore, it turned out that selective disubstitution with **14** occurred through intramolecular transfer of PdP^tBu₃ on the longer conjugated π-faces including C=C of polystilbene (10 benzene rings and 5 C=C's are included in polystilbene with an M_n of 4000). When the same reaction was carried out in the presence of 10 mol % stilbene as an additive to disturb intramolecular

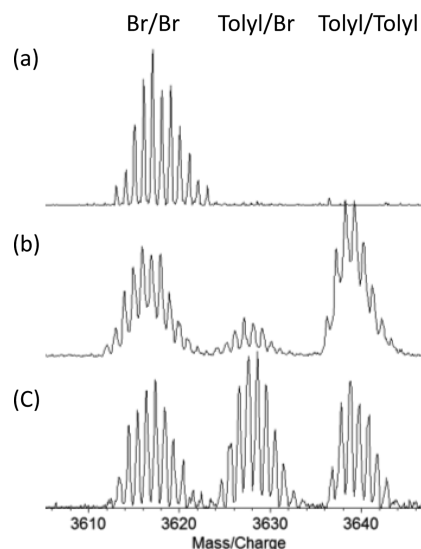
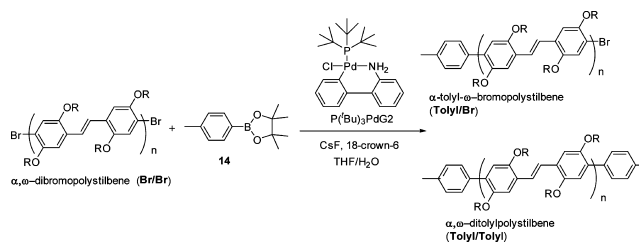


Figure 1. MALDI-TOF mass spectra of products of (a) α,ω-dibromo polystilbene (M_n = 4010, M_w/M_n = 1.66), (b) polystilbene (M_n = 4290, M_w/M_n = 1.65) obtained by reaction of α,ω-dibromo polystilbene with **14** in the presence of CsF/18-crown-6 and 10 mol % P(^tBu)₃PdG2 in THF/H₂O at room temperature for 7.5 h, and (c) polystilbene (M_n = 6650, M_w/M_n = 1.60) obtained by reaction of α,ω-dibromo polystilbene with **14** under the same conditions of (b) in the presence of 10 mol % stilbene.

Scheme 3. Model Reaction of α,ω-Dibromo Polystilbene with Equimolar **14**



transfer of the Pd catalyst, the MALDI-TOF mass spectrum of the products was dramatically changed, and the Br/Tolyl peaks became major (Figure 1c). This result also supports the occurrence of intramolecular transfer of the Pd catalyst on the long conjugated polystilbene backbone in the Suzuki–Miyaura coupling reaction of α,ω-dibromo polystilbene with **14**.

The structural requirements for intramolecular transfer of ^tBu₃PPd(0) on C=C were established by examination of the Suzuki–Miyaura coupling reaction of dibromostilbenes with aryl boronic acid esters as a model reaction of CTCP. Substituent groups at the ortho position of C=C are critical for selective intramolecular transfer of the catalyst; they may serve to suppress the formation of the bimolecular C=C–Pd–C=C complex that leads to intermolecular transfer of PdP^tBu₃. We believe the present findings will be useful in the design of CTCP reactions of monomers containing C=C and also represent an advance in our understanding of organic/organometallic chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experiment and ¹H NMR, ¹³C NMR, MALDI-TOF MS. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03113.

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Notes

The authors declare no competing financial interest.

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