Reaction of *trans*-Pd(styryl)Br(PMePh$_2$)$_2$ with Styryl Bromide Affording 1,4-Diphenylbutadiene. An Unexpected Homocoupling Process Induced by P−C Reductive Elimination

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Reaction of (*Z*)-styryl bromide (**1**) with PhB(OH)$_2$ in toluene at 80 °C for 1 h in the presence of Pd(PPh$_3$)$_4$ (1.5 mol %) and an aqueous solution of K$_2$CO$_3$ (3 equiv) affords (*Z*)-stilbene as the cross-coupling product in 99% yield. On the other hand, the same reaction of the (*E*)-isomer of **1** forms considerable amounts of homocoupling products (1,4-diphenylbutadiene (**2**, 22%) and biphenyl (27%)) in addition to the cross-coupling product ((*E*)-stilbene, 73%). The formation of **2** was examined by kinetic experiments using *trans*-Pd(CH=CHPh)Br(PMePh$_2$)$_2$ (**3**) as a model of the presumed intermediate. Complex **3** reacts with **1** at 50 °C for 5 h, giving **2** (91%) and *trans*-PdBr$_2$(PMePh$_2$)$_2$ (**4**, 92%), together with a small amount of Pd(η^2-PhCH=CHPMePh$_2$)Br(PMePh$_2$) (**5**, 8%). The reaction rate shows first-order dependence on the concentration of **3** and **5**, respectively, but is independent of the concentration of **1**. A novel homocoupling process induced by P−C reductive elimination from **3** giving **5** is proposed.

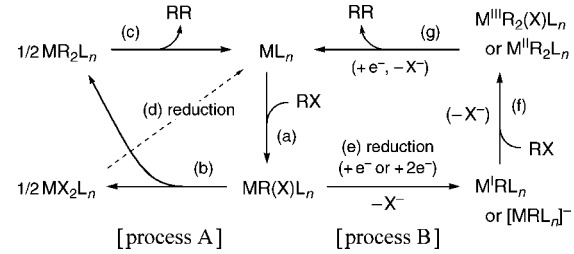
Introduction

Dehalogenative homocoupling of aryl and alkenyl halides promoted by nickel[1] and palladium[2] complexes is a useful means of C−C bond formation,[3] especially for the synthesis of π-conjugated polymers.[4] This reaction also takes place quite often as a side reaction of the catalytic cross-coupling of organic halides with organometallic reagents.[5,6]

Scheme 1 illustrates a schematic view of homocoupling processes previously reported. The first step is oxidative addition of organic halides (RX) to low-valent transition metal species (ML$_n$) (step a). The resulting MR(X)L$_n$ may undergo two reaction processes (A and B) affording homocoupling products (RR). Process A involves metathesis of MR(X)L$_n$ to give MR$_2$L$_n$ and MX$_2$L$_n$ (step b).[7] The former forms RR on reductive elimination (step c), whereas the latter is reduced to ML$_n$ when the reaction is conducted in catalytic systems containing reducing agents such as zinc and organometallic reagents (step d). This type of process was first documented by Tsou and Kochi for a nickel system using aryl bromides (ArBr) as substrates, where intermolecular exchange of aryl and bromo ligands between diamagnetic Ni^{II}Br(Ar)(PEt$_3$)$_n$ and paramagnetic Ni^{III}Br$_2$(Ar)(PEt$_3$)$_n$ was postulated to afford Ni^{III}(Br)Ar$_2$(PEt$_3$)$_n$ and Ni^{II}Br$_2$(PEt$_3$)$_n$.[8] More recently, Osakada and Yamamoto examined metathesis of diamagnetic MAr(X)(bipy) complexes (M = Ni, Pd) in detail and demonstrated high reactivity of cationic [MAr(bipy)]$^+$ species.[9]

On the other hand, process B involves oxidative addition of RX to paramagnetic M^{I}RL$_n$ or anionic [MRL$_n$]$^-$ species generated by

Scheme 1



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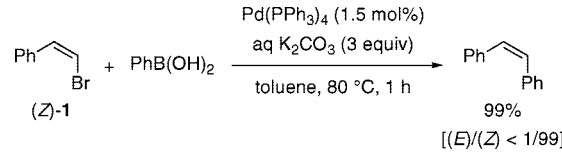
chemical or electrochemical reduction of $MR(X)L_n$ (step e → step f).[10] The reaction forms $M^{III}R_2(X)L_n$ or MR_2L_n, which reductively eliminates RR (step g). This type of process was originally proposed for nickel-catalyzed reactions by Colon and Kelsey[10] and expanded to palladium-catalyzed systems by Amatore and Jutand.[11]

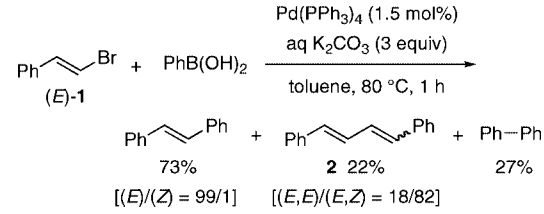
This paper deals with the homocoupling process of styryl bromide promoted by palladium(0) phosphine complexes. In the course of our study on stereocontrolled synthesis of poly(phenylene vinylene) (PPV) using the Suzuki−Miyaura cross-coupling,[12] we found that the (*Z*,*Z*)-isomer of bis(2-bromoethenyl)benzene cleanly forms PPV, whereas the corresponding (*E*,*E*)-isomer provides a polymer containing a notable amount of butadiene unit in the main chain resulting from homocoupling.[13] In this context, we attempt in this study to clarify the following points using a model reaction of isolated *trans*-Pd(CH=CHPh)Br($PMePh_2$)$_2$ (**3**)[14] with styryl bromide to give 1,4-diphenylbutadiene: (i) the effect of (*E*)/(*Z*) configuration of the styryl group; (ii) the mechanism of the homocoupling process. It has been found that the butadiene formation proceeds via a novel homocoupling process induced by P−C reductive elimination from **3** to give Pd(η^2-PhCH=CHP$MePh_2$)-Br($PMePh_2$) (**5**).[15]

Results

Effect of (*E*)/(*Z*) Configuration of the Styryl Group. Cross-coupling reactions of (*Z*)- and (*E*)-styryl bromides (**1**) with $PhB(OH)_2$ were examined under the catalytic conditions for PPV synthesis. Thus a 1:1 mixture of **1** and $PhB(OH)_2$ was heated at 80 °C for 1 h in toluene in the presence of $Pd(PPh_3)_4$ (1.5 mol %) and an aqueous solution of K_2CO_3 (3 equiv). In agreement with the polymerization results, (*Z*)-**1** selectively underwent cross-coupling, giving (*Z*)-stilbene in quantitative yield (eq 1). On the other hand, the reaction of (*E*)-**1** afforded considerable amounts of homocoupling products (i.e., 1,4-diphenylbutadiene (**2**, 22%) and biphenyl (27%)), along with (*E*)-stilbene as the cross-coupling product (73%) (eq 2). It should be noted that butadiene **2** contains a significant amount of (*E*,*Z*)-isomer in addition to the (*E*,*E*)-isomer that is expected from the geometry of starting (*E*)-**1**. Since the cross-coupling product retains totally the original (*E*) configuration, it is likely that the (*E*)/(*Z*) isomerization of styryl group takes place uniquely in the homocoupling process.

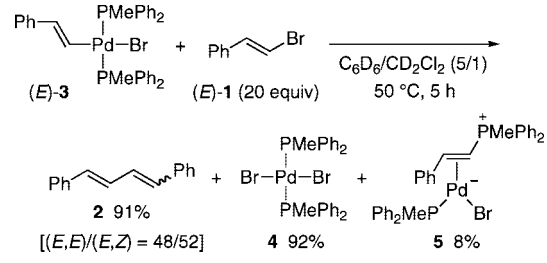


(1)



(2)

Next, we examined the homocoupling reaction giving **2** in stoichiometric systems using *trans*-Pd(CH=CHPh)Br($PMePh_2$)$_2$ (**3**) bearing (*Z*)- and (*E*)-styryl groups. While the $PMePh_2$ complexes were employed instead of PPh_3 analogues for solubility reason, their reactions with styryl bromides faithfully reproduced the characteristic points observed in the catalytic systems. Thus, (*Z*)-**3** was almost unreactive to (*Z*)-styryl bromide ((*Z*)-**1**).[16] On the other hand, (*E*)-**3** smoothly reacted with (*E*)-styryl bromide ((*E*)-**1**, 20 equiv) in C_6D_6/CD_2Cl_2 (5:1) at 50 °C for 5 h to afford a geometrical mixture of 1,4-diphenylbutadiene (**2**, (*E*,*E*)/(*E*,*Z*) = 48/52, totally 91%), together with *trans*-$PdBr_2(PMePh_2)_2$ (**4**, 92%) (eq 3). Accordingly, (i) much higher reactivity of (*E*)-styryl isomer than (*Z*)-styryl isomer toward homocoupling and (ii) the occurrence of (*E*)/(*Z*) isomerization of styryl group during the homocoupling process were evidenced in the stoichiometric systems as well. As described below, the remaining part of (*E*)-**3** (8%) is converted to styrylphosphonium complex **5**, which is formed by P−C reductive elimination of styryl and $PMePh_2$ ligands.[15,17]



(3)

Kinetic Examination of the Homocoupling Mechanism. Figure 1 shows the time-course of eq 3. Palladium dibromide **4** forms at the expense of (*E*)-**3**. At the same time, complex **5** increases, while this complex is converted at the final stage to

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(16) (a) Treatment of (*Z*)-**3** with (*Z*)-**1** (20 equiv) in C_6D_6/CD_2Cl_2 (5:1) at 50 °C for 5 h gave a small amount of *trans*-$PdBr_2(PMePh_2)_2$ (**4**, ca. 2%), while most of (*Z*)-**3** remained unreacted. GLC analysis revealed no formation of 1,4-diphenylbutadiene (**2**). (b) Complex (*Z*)-**3** was stable at 50 °C for 5 h in C_6D_6 in the presence of (*E*)-**1** (20 equiv).

(17) (a) Heating (*E*)-**3** in C_6D_6 at 50 °C for 6 h resulted in the formation of **5** in 52% yield as confirmed by NMR spectroscopy. Also formed in the solution are butadiene **2** ((*E*,*E*)/(*E*,*Z*) = 48/52, 23%) and dibromopalladium **4** (8%). (b) Unlike (*E*)-**3**, (*Z*)-**3** was stable in C_6D_6 at 50 °C for 6 h.

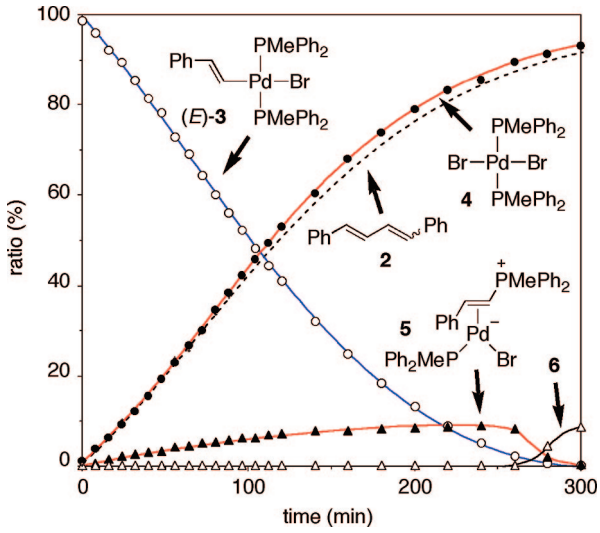


Figure 1. Time course of the reaction of (*E*)-**3** (50 mM) with (*E*)-**1** (1.0 M) in C_6D_6/CD_2Cl_2 (5:1 v/v) at 50 °C. Palladium complexes **3**–**6** and butadiene (**2**) were followed by ^1H NMR spectroscopy.

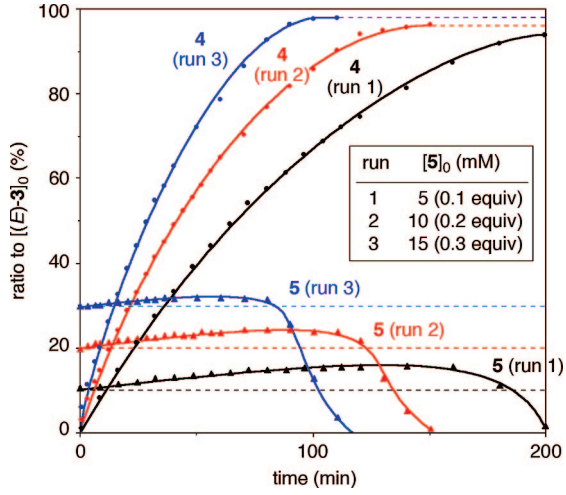


Figure 2. Time course of the reaction of (*E*)-**3** (50 mM) with (*E*)-**1** (1.0 M) in C_6D_6/CD_2Cl_2 (5:1 v/v) at 50 °C in the presence of isolated **5**.

the other palladium species **6**[18] with liberation of $[PhCH{=}CHPMePh_2]^+Br^-$ (**7**). It was confirmed that the amount of butadiene **2** is consistent with that of **4** through the reaction. Clearly, the reaction curves for the conversion of (*E*)-**3** and the formation of **4** are S-shaped, showing the occurrence of an autocatalytic process. Since the reaction is apparently accelerated as the amount of **5** increases, we next investigated the reaction of (*E*)-**3** with (*E*)-**1** in the presence of added **5**. Complex **5** was prepared separately according to the procedure reported for PPh_3 analogues.[15c]

Figure 2 shows the time course in the presence of added **5**, where the amounts of **4** and **5** are based on the amount of (*E*)-**3** initially employed ($[(E)\text{-}\mathbf{3}]_0 = 50$ mM). Both the yield and the formation rate of **4** are enhanced by addition of **5** to the system ($[\mathbf{5}]_0 = 5$–15 mM, runs 1–3). Furthermore, the amount of **5** generated from (*E*)-**3** during the reaction clearly decreases as

Table 1. Kinetic Data for Formation of 4 in the Reactions of (*E*)-3 and (*E*)-1[a]

run	$[\mathbf{5}]_0$ (mM)	10^4k_1 (s^{-1})[b]	10^2k_2 (s^{-1} M^{-1})[c]
0[d]	0		2.5(1)[e]
1	5	1.80(2)	2.37(2)
2	10	2.72(2)	2.36(2)
3	15	3.86(6)	2.54(4)

[a] Reaction conditions: $[(E)\text{-}\mathbf{3}]_0 = 50$ mM, $[(E)\text{-}\mathbf{1}]_0 = 1.0$ M, in C_6D_6/CD_2Cl_2 (5:1), at 50 °C. [b] Estimated by regression analysis of the kinetic data (up to 63% conversion of (*E*)-**3**) using the following equation: $\ln\{[(E)\text{-}\mathbf{3}]_0/([(E)\text{-}\mathbf{3}]_0 - [\mathbf{4}]_t)\} = k_1t$. [c] Estimated by regression analysis of the kinetic data (up to 83% conversion of (*E*)-**3**) using the following equation: $\ln\{[(E)\text{-}\mathbf{3}]_0/([(E)\text{-}\mathbf{3}]_0 - [\mathbf{4}]_t)\} = k_2([\mathbf{5}]_t \times t)$. [d] Data for Figure 1. [e] Data for less than 20% conversion of (*E*)-**3** were omitted from the calculation because the concentration of **5** was too low to be accurately analyzed (<3%).

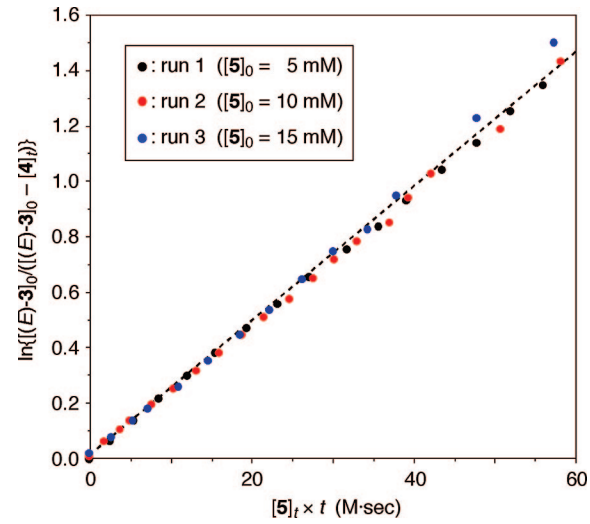


Figure 3. Plot of $\ln\{[(E)\text{-}\mathbf{3}]_0/([(E)\text{-}\mathbf{3}]_0 - [\mathbf{4}]_t)\}$ vs $([\mathbf{5}]_t \times t)$ for the reactions of Figure 2.

the amount of added **5** increases.[19] It should be noted that the time−yield curves for **4** have a simple form (not S-shaped). Actually, the reactions obeyed first-order kinetics up to 63% conversion of (*E*)-**3**.

Table 1 lists the first-order rate constants (k_1) thus obtained. The k_2 values in the fourth column are second-order rate constants estimated by applying kinetic data to the following equation: $\ln\{[(E)\text{-}\mathbf{3}]_0/([(E)\text{-}\mathbf{3}]_0 - [\mathbf{4}]_t)\} = k_2([\mathbf{5}]_t \times t)$. Thus, since the gradual formation of **5** from (*E*)-**3** could not be ignored even in the presence of added **5**, the formation rate of **4** was compensated for the concentration of **5** at time *t*. This treatment resulted in good linear correlations for all runs up to 83% conversion of (*E*)-**3**, giving almost identical k_2 values ($2.4(1) \times 10^{-2}$ s^{-1} M^{-1}) (Figure 3). Hence the first-order dependence of the reaction rate on the concentration of (*E*)-**3** and **5**, respectively, was confirmed: $d[\mathbf{4}]/dt = k_2[(E)\text{-}\mathbf{3}][\mathbf{5}]$.

Table 2 compares half-lives of (*E*)-**3** under various conditions. The reaction is highly sensitive to solvent polarity and clearly faster in a polar solvent (runs 1–3; runs 4 and 5). On the other hand, the reaction rate is less sensitive to the concentration of (*E*)-styryl bromide ((*E*)-**1**) (runs 1 and 4; runs 2 and 5). Although small variations of half-lives are observed depending on the concentration of (*E*)-**1**, they are attributable to the change in polarity of reaction media. Thus, in C_6D_6 as a nonpolar solvent,

(18) Although **6** could not be isolated, it was assigned as $[Pd(CH{=}CHPh)(\mu\text{-}Br)(PMePh_2)]_2$ based on the similarity of NMR data [^1H NMR: δ 2.14 (d, $^2J_{HP} = 11.4$ Hz, PCH_3); $^{31}P\{^1H\}$ NMR: δ 15.2 (s)] to related $[PdR(\mu\text{-}Cl)(PMePh_2)]_2$ (R = Ph, CH_2Ph). Anderson, G. K. *Organometallics* **1983**, *2*, 665–668.

(19) (a) The yield of **4** in each run of Figure 2(%): 94 (run 1), 96 (run 2), 98 (run 3). (b) The maximum amount of **5** derived from (*E*)-**3** (%): 6 (run 1), 4 (run 2), 2 (run 3). Complex **5** was converted to **6** and **7** at the final stage as described for Figure 1.

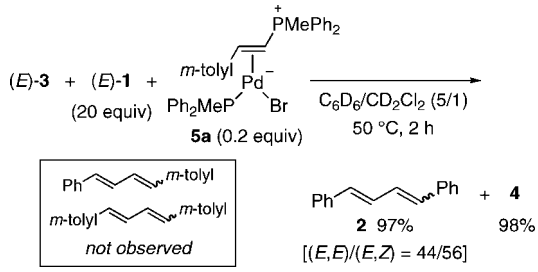
Table 2. Half-Lives of (*E*)-3 in Reactions with (*E*)-1[a]

run	$[(E)\text{-}\mathbf{1}]_0$ (M)	solvent	additive	$t_{1/2}$ (min)
1	1.0	C_6D_6		200
2	1.0	C_6D_6/CD_2Cl_2 (5/1)		100
3	1.0	C_6D_6/CD_2Cl_2 (1/1)		48
4	0.50	C_6D_6		240
5	0.50	C_6D_6/CD_2Cl_2 (5/1)		76
6	1.0	C_6D_6/CD_2Cl_2 (5/1)	$PMePh_2$ (5 mM)	280
7	1.0	C_6D_6/CD_2Cl_2 (5/1)	**7** (1.5 mM)[b]	130

[a] Reaction conditions: $[(E)\text{-}\mathbf{3}]_0$ = 50 mM, at 50 °C. [b] **7**: $[PhCH{=}CHPMePh_2]^+Br^-$.

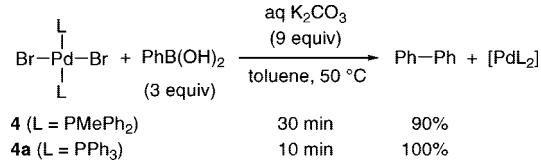
the reaction is faster at higher concentration of (*E*)-**1**, because (*E*)-**1** possesses higher polarity than benzene (run 1 > run 4). To the contrary, the higher concentration of (*E*)-**1** makes the reaction slower when the reaction solution contains CD_2Cl_2 as a highly polar solvent (run 2 < run 5). Accordingly, it is concluded that the rate of homocoupling (i.e., the formation of butadiene **2**) is essentially independent of the concentration of (*E*)-styryl bromide ((*E*)-**1**). As seen from runs 6 and 7, the reaction is retarded by free $PMePh_2$ and $[PhCH{=}CHPMePh_2]^+Br^-$ (**7**), respectively, while the effect of **7** is small.

Labeling Experiment. The kinetic experiments revealed a crucial role of styrylphosphonium complex **5** in the homocoupling process. In this connection, the reaction of (*E*)-**3** with (*E*)-**1** was examined in the presence of $Pd(\eta^2\text{-}m\text{-}MeC_6H_4CH{=}CHPMePh_2)Br(PMePh_2)$ (**5a**, 0.2 equiv, 10 mM) in place of **5**. As shown in eq 4, the reaction gave 1,4-diphenylbutadiene **2** and palladium dibromide **4** in almost quantitative yields. Thus, the *m*-$MeC_6H_4CH{=}CH$ group of **5a** was not incorporated into the product.



(4)

Relation between Stoichiometric and Catalytic Reactions. The reaction of styryl complex (*E*)-**3** with (*E*)-styryl bromide ((*E*)-**1**) afforded butadiene **2** and palladium dibromide **4** in over 90% yields (eq 3). When this reaction proceeds catalytically, **4** should be reduced to a Pd(0) species, which subsequently undergoes oxidative addition of (*E*)-**1** to reproduce (*E*)-**3**. Since the catalytic reaction in eq 2 formed a comparable amount of biphenyl along with **2**, it is likely that $PhB(OH)_2$ serves as a reducing agent in conjunction with a base. In fact, complex **4** smoothly reacted with $PhB(OH)_2$ (3 equiv) in toluene in the presence of an aqueous solution of K_2CO_3 (9 equiv) (eq 5). The reaction was completed in 30 min at 50 °C to give biphenyl in 90% yield. Similarly, the PPh_3 complex **4a** formed a quantitative yield of biphenyl in 10 min. The observed reactivity of **4a** was high enough to be operative as an elementary process in the catalytic conversion of (*E*)-**1**.



(5)

Discussion

The following points have emerged from the experimental results. (1) (*Z*)-styryl bromide ((*Z*)-**1**) is much less reactive than the corresponding (*E*)-isomer ((*E*)-**1**) toward dehalogenative homocoupling, giving 1,4-diphenylbutadiene (**2**), because the (*Z*)-styrylpalladium intermediate ((*Z*)-**3**) is sufficiently stable toward P−C reductive elimination. (2) In contrast, (*E*)-styrylpalladium ((*E*)-**3**) readily undergoes P−C reductive elimination to give styrylphosphonium complex (**5**), which induces the reaction of (*E*)-**3** with (*E*)-**1** to afford **2** and palladium dibromide **4**. (3) The homocoupling reaction involves (*E*)/(*Z*) isomerization of the styryl group to give a mixture of (*E*,*E*)- and (*E*,*Z*)-isomers of **2**. (4) The rate of formation of **2** and **4** shows first-order dependence on the concentration of (*E*)-**3** and **5**, respectively, but is independent of the concentration of (*E*)-**1**. (5) A polar solvent accelerates the reaction, whereas free $PMePh_2$ and $[PhCH{=}CHPMePh_2]^+Br^-$ (**7**) retard the reaction. (6) The styryl group of styrylphosphonium complex **5** is not incorporated into the homocoupling product (**2**). (7) Palladium dibromide (**4** or **4a**) readily reacts with $PhB(OH)_2$ in the presence of aqueous K_2CO_3 to afford biphenyl and a Pd(0) species.

Taking these observations into account, we propose the mechanism in Scheme 2 for the conversion of (*E*)-**1** and (*E*)-**3** into **2** and **4**, which consists of initiation (steps a, b) and production (steps c, d) processes. First, styryl complex (*E*)-**3** undergoes P−C reductive elimination to give styrylphosphonium complex **5** (step a). Unlike the arylpalladium analogues $(PdAr^1(X)(PAr^2_3)_2$; Ar^1, Ar^2 = Ph, *p*-tolyl, etc.),[20] the P−C coupling proceeds irreversibly, as confirmed by the labeling experiment in eq 4. Complex **5** then reacts with styryl bromide ((*E*)-**1**) to afford a three-coordinated complex **A** with liberation of $[PhCH{=}CHPMePh_2]^+Br^-$ (**7**) (step b).[21]

Complex **A** serves as a key intermediate in the production process. Intermolecular exchange of the styryl ligand in **A** and the bromo ligand in (*E*)-**3** forms bis(styryl) complex **B** and dibromo complex **4** (step c). Reductive elimination of **2** from **B**, followed by oxidative addition of (*E*)-**1** to a resulting Pd(0) species, regenerates **A** (step d). Accordingly, **A** catalyzes the conversion of (*E*)-**1** and (*E*)-**3** into **2** and **4**. In this case, since the reaction rate is independent of the concentration of (*E*)-**1**, step d must be much faster than step c. This situation is very convincing because the C−C reductive elimination from related *cis*-$Pd(CH{=}CHPh)(Me)(PMePh_2)_2$ and the oxidative addition of (*E*)-styryl bromide to a Pd(0) phosphine complex proceed readily even at room temperature.[14,22]

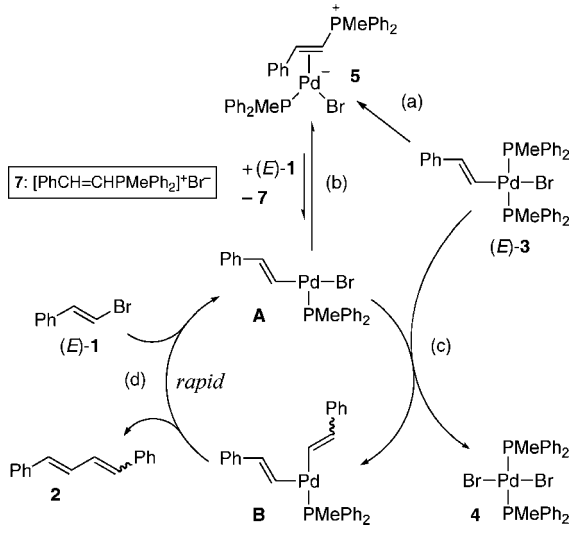
The reaction rate showed first-order dependence on the concentration of (*E*)-**3** and **5**, respectively. Apart from (*E*)-**3** as the substrate of step c, the kinetic relation of **5** to the production

(20) Aryl complexes undergo reversible P−C reductive elimination leading to intramolecular exchange of the $PdAr^1$ and PAr^2 groups: (a) Kong, K.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6313–6315. (b) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441–12453. (c) Grushin, V. V. *Organometallics* **2000**, *19*, 1888–1900. (d) Grushin, V. V. *Chem.−Eur. J.* **2002**, *8*, 1006–1014. (e) Grushin, V. V. *Organometallics* **2007**, *26*, 4997–5002.

(21) T-shaped, three-coordinated complexes have been isolated for arylpalladium halides: (a) Stambuli, J. P.; Buhl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9346–9347. (b) Stambuli, J. P.; Incarvito, C. D.; Buhl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 1184–1194.

(22) (a) Brown, J. M.; Cooley, N. A. *Organometallics* **1990**, *9*, 353–359. (b) Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431–1438. (c) Ozawa, F. In *Current Methods in Inorganic Chemistry*; Yamamoto, A., Kurosawa, H., Eds.; Elsevier: Amsterdam, 2003; Vol. 3,Chapter 9.

Scheme 2



process deserves discussion. It is assumed that **5** is converted to **A** and **7** by reaction with (*E*)-**1**. In fact, **7** is generated in the system at the final reaction stage, along with **6** as a dimer of **A** (Figure 1). However, since **6** and **7** are not observed in the early to middle stage of the reaction, it must be considered that **5** and **A** are rapidly interconverted, and the equilibrium lies far on the side of **5**.[23] In this situation, complex **5** remains apparently unchanged in the reaction system, because **A** is recycled as catalyst in the production process and therefore its concentration is maintained. On the other hand, when (*E*)-**3**is almost completely consumed at the final stage, **A** is dimerized to a stable form, to be converted entirely to **6** and **7**.

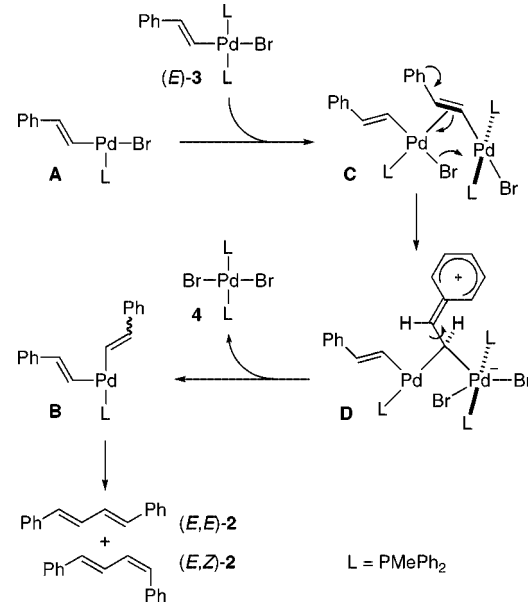
The 1,4-diphenylbutadiene (**2**) was obtained as a mixture of (*E*,*E*)- and (*E*,*Z*)-isomers. Since (*Z*)-styryl complex ((*Z*)-**3**) was not observed in the system during the reaction, the (*E*)/(*Z*) isomerization of the styryl group should be operative in step c in Scheme 2, causing intermolecular exchange of the styryl ligand in (*E*)-**3** and the bromo ligand in **A**. Scheme 3 illustrates a plausible mechanism responsible for this phenomenon. The first step is very probably η^2-coordination of the styryl ligand of (*E*)-**3** to the vacant coordination site of **A**. The styryl ligand then changes its coordination to an η^1-fashion, in conjunction with the transfer of bromo ligand in least motion. This change in coordination mode of the styryl ligand provides intermediate **D** involving a contribution of the canonical structure given in Scheme 3, in which free rotation of the μ-styryl ligand is possible. Accordingly, the two geometrical isomers of **2** are formed.

Conclusion

We have demonstrated a novel homocoupling process of (*E*)-styryl bromide promoted by palladium(0) phosphine complexes. Thus the reaction of (*E*)-styryl complex ((*E*)-**3**) with (*E*)-styryl bromide ((*E*)-**1**) is promoted by a catalytic amount of coordinatively unsaturated complex **A**, which is generated by P−C

(23) A polar solvent increases the equilibrium concentration of **A** and **7**, causing enhancement in the reaction rate. On the other hand, addition of **7** to the system decreases the concentration of **A** and reduces the reaction rate. The retardation effect of free $PMePh_2$ may be attributed to several reasons. For example, intermediate **A** is very probably captured as (*E*)-**3**. Furthermore, since complex **5** is converted to $[Pd(\eta^2\text{-PhCH=CHPMePh}_2)(PMePh_2)_2]^+Br^-$ by the coordination of $PMePh_2$, the formation of **A** is possibly hindered by increasing coordination stability of the styrylphosphonium ligand.

Scheme 3



reductive elimination of the styryl and $PMePh_2$ ligands from (*E*)-**3**, followed by oxidative addition of (*E*)-**1** to resulting styrylphosphonium complex **5**. We have also shown that (*E*)/(*Z*) isomerization of the styryl group, which takes place during the formation of 1,4-diphenylbutadiene (**2**), is reasonably accounted for by a mechanism involving intermolecular exchange of the styryl ligand between **A** and (*E*)-**3**.

Dehalogenative homocoupling catalyzed by palladium complexes has been examined mainly for the reactions with aryl halides as substrates.[2] Process B in Scheme 1 is currently most accepted for such reactions, where oxidative addition of aryl halides to anionic $[MRL_n]^-$ intermediates formed by two-electron reduction of $MR(X)L_n$ is considered.[11] In contrast, we found a considerably different type of process for the reaction of (*E*)-styryl bromide ((*E*)-**1**) to give 1,4-diphenylbutadiene (**2**). The C−C coupling process proposed in Scheme 2 resembles our previous observations for the reactions of *trans*-$PdAr_2L_2$ with RX (R = Me, aryl; L = PEt_2Ph), where *trans*-$PdR(X)L_2$ formed by oxidative addition of RX to a palladium(0) species catalyzes the conversion of *trans*-$PdAr_2L_2$ and RX into ArR.[24]

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk techniques. Nitrogen and argon gas were dried by passing through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H NMR 400.13 MHz, ^{13}C NMR 100.62 MHz, and ^{31}P NMR 161.97 MHz). Chemical shifts are reported in δ (ppm), referenced to the ^{1}H (residual protons), and ^{13}C signals of deuterated solvents or to the ^{31}P signal of an external 85% H_3PO_4 standard. Mass spectra were measured on a Shimadzu GC-MS QP2010 spectrometer (EI, 70 eV). GLC analysis was performed on a Shimadzu GC-14B instrument equipped with a FID detector and a CBP-1 capillary column (25 m × 0.25 mm). Melting points were measured with a Yanaco MP-S3 instrument. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University.

(24) (a) Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144–2149. (b) Ozawa, F.; Hidaka, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *330*, 253–263.

Toluene was dried over sodium benzophenone ketyl, distilled, and stored over activated molecular sieves (MS4A). C_6D_6 and CD_2Cl_2 were dried over lithium aluminum hydride (for C_6D_6) or calcium hydride (for CD_2Cl_2), transferred under vacuum, and stored over activated molecular sieves (MS4A). Et_2O, THF, and CH_2Cl_2 (Wako, dehydrated) were used as received. (*E*)-Styryl bromide ((*E*)-**1**) was purified in an alkaline condition to remove contamination of the (*Z*)-isomer.[25]The following compounds were synthesized according to the literature: (*Z*)-styryl bromide ((*Z*)-**1**),[26] $Pd(PPh_3)_4$,[27](*Z*)-*trans*-$Pd(CH{=}CHPh)Br(PMePh_2)_2$ ((*Z*)-**3**),[14a] *trans*-$PdBr_2(PMePh_2)_2$ (**4**),[28] *trans*-$PdBr_2(PPh_3)_2$ (**4a**).[29]

Synthesis of (*E*)-*trans*-Pd(CH═CHPh)Br(PMePh$_2$)$_2$ ((*E*)-3). $PMePh_2$ (411 mg, 2.05 mmol) was added to a solution of (η^5-C_5H_5)(η^3-C_3H_5)Pd[30] (213 mg, 1.00 mmol) in toluene (1.0 mL) at 0 °C. The mixture was stirred for 10 min, and (*E*)-**1** (732 mg, 4.00 mmol) was added. The homogeneous solution was stirred at room temperature, causing gradual precipitation of a white solid. After 3 h, hexane (5 mL) was added, and the mixture was cooled to −20 °C. The white precipitate formed in the system was collected by filtration, washed successively with hexane (2 × 2 mL) and Et_2O (2 × 2 mL), and dried under vacuum. The crude product was purified by recrystallization from CH_2Cl_2/Et_2O at room temperature, washed with Et_2O, and dried under vacuum at 0 °C to afford pale brown crystals of the title compound (603 mg, 87% yield). The NMR data were identical with those reported.[14b] ^{1}H NMR (CD_2Cl_2): δ 7.65–7.58 and 7.45–7.35 (m, 20H in total), 7.05 (m, 2H), 6.93 (m, 1H), 6.54 (tt, $^3J_{HH}$ = 16.0 Hz, $^3J_{HP}$ = 9.6 Hz, 1H), 6.47 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 5.64 (dt, $^3J_{HH}$ = 16.0 Hz, $^4J_{HP}$ = 1.9 Hz, 1H), 2.07 (virtual triplet, J = 3.3 Hz, 6H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 7.8 (s).

Synthesis of (*E*)-[PhCH═CHPMePh$_2$]Br (7). This compound was prepared by the procedure reported for (*E*)-[PhCH═CHPPh$_3$]Br.[15c] A solution of (*E*)-**1** (802 mg, 4.38 mmol) and $PMePh_2$ (878 mg, 4.38 mmol) in toluene (22 mL) was stirred at 100 °C in the presence of $Pd(PMePh_2)_4$[31] (199 mg, 0.219 mmol) for 24 h. The white precipitate formed in the system was collected by filtration, washed with hexane and Et_2O, and dried under vacuum (1.57 g, 94%). Mp: 181–183 °C. ^{1}H NMR ($CDCl_3$): δ 7.89–7.74, 7.70–7.65, and 7.51–7.37 (m, 17H in total), 3.06 (d, $^2J_{HP}$ = 13.7 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.9 (d, $^3J_{PC}$ = 4.7 Hz), 134.7 (d, $^4J_{PC}$ = 3.0 Hz), 133.6 (d, $^2J_{PC}$ = 20.3 Hz), 132.9 (d, $^3J_{PC}$ = 10.5 Hz), 131.9 (s), 130.2 (d, $^2J_{PC}$ = 12.7 Hz), 129.2 (s), 129.1 (s), 119.7 (d, $^1J_{PC}$ = 89.7 Hz), 106.4 (d, $^1J_{PC}$ = 89.0 Hz), 10.7 (d, $^1J_{PC}$ = 58.5 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 19.6 (s). Anal. Calcd for $C_{21}H_{20}BrP$: C, 65.81; H, 5.26. Found: C, 65.58; H, 5.32.

(*E*)-[*m*-$MeC_6H_4CH{=}CHPMePh_2$]Br (**7a**) was similarly prepared as a white powder by the reaction of (*E*)-*m*-methylstyryl bromide (312 mg, 1.58 mmol) and $PMePh_2$ (317 mg, 294 mmol) in toluene (8 mL) in the presence of $Pd(PMePh_2)_4$ (71.8 mg, 0.0791 mmol) (585 mg, 93%). Mp: 138–140 °C. ^{1}H NMR ($CDCl_3$): δ 7.88–7.76 and 7.72–7.55 (m, 13H in total), 7.40 (dd, $^3J_{HP}$ = 23.1 Hz, $^3J_{HH}$ = 17.4 Hz, 1H), 7.34–7.27 (m, 2H), 3.10 (d, $^2J_{HP}$ = 13.7 Hz, 3H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.2 (d, $^3J_{PC}$ = 4.4 Hz), 138.9 (s), 134.7 (d, $^4J_{PC}$ = 2.9 Hz), 133.5 (d, $^2J_{PC}$ = 20.1 Hz), 132.9 (d, $^3J_{PC}$ = 10.8 Hz), 132.8 (s), 130.2 (d, J = 12.9 Hz), 129.7 (s), 129.0, (s), 126.4 (s), 119.8 (d, $^1J_{PC}$ = 89.5 Hz), 105.9 (d, $^1J_{PC}$ = 89.3 Hz), 21.2 (s), 10.7 (d, $^1J_{PC}$ = 58.5 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 19.6 (s). Anal. Calcd for $C_{22}H_{22}BrP$: C, 66.51; H, 5.58. Found: C, 66.62; H, 5.67.

Synthesis of Pd(η^2-PhCH═CHPMePh$_2$)Br(PMePh$_2$) (5). To a solution of $PMePh_2$ (128 mg, 0.639 mmol) in CH_2Cl_2 (6.4 mL) were added $Pd(dba)_2$[32] (368 mg, 0.639 mmol) and **7** (245 mg, 0.639 mmol). The solution was stirred at room temperature for 3 h and filtered through a Celite pad. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (3 mL) and diluted with Et_2O (10 mL), and a green solid formed in the solution was removed by filtration. This operation was repeated three times to give a crude product (255 mg, 58% yield). Recrystallization from CH_2Cl_2/Et_2O at −30 °C gave yellow crystals of the title compound (224 mg, 51% yield). Mp: 126–128 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 8.04–7.97, 7.75–7.42, 7.24–6.86, and 6.81–6.78 (m, 25H in total), 3.34 (ddd, $^2J_{HP}$ = 19.8 Hz, $^3J_{HH}$ = 10.7 Hz, $^3J_{HP}$ = 4.1 Hz, 1H), 3.12 (ddd, $^3J_{HP}$ = 14.0 Hz, $^3J_{HH}$ = 10.7 Hz, $^3J_{HP}$ = 8.2 Hz, 1H), 2.83 (d, $^2J_{HP}$ = 13.7 Hz, 3H), 1.50 (d, $^2J_{HP}$ = 6.2 Hz, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 144.8 (d, $^3J_{PC}$ = 11.4 Hz), 139.3 (d, $^1J_{PC}$ = 28.1 Hz), 137.0 (d, $^1J_{PC}$ = 29.4 Hz), 134.9 (d, $^3J_{PC}$ = 10.1 Hz), 133.5 (s), 134.8 (s), 132.8 (d, $^2J_{PC}$ = 14.4 Hz), 132.6 (d, $^3J_{PC}$ = 9.9 Hz), 132.5 (d, $^2J_{PC}$ = 14.0 Hz), 129.9 (d, $^2J_{PC}$ = 11.3 Hz), 129.2 (s), 129.1 (d, $^2J_{PC}$ = 12.4 Hz), 128.9 (d, $^4J_{PC}$ = 1.2 Hz), 128.7 (s), 128.4 (d, $^3J_{PC}$ = 9.0 Hz), 128.2 (d, $^3J_{PC}$ = 9.1 Hz), 127.4 (dd, $^1J_{PC}$ = 72.7 Hz, $^4J_{PC}$ = 9.5 Hz), 125.7 (s), 124.9 (s), 124.9 (d, $^1J_{PC}$ = 93.3 Hz), 59.5 (d, $^2J_{PC}$ = 5.0 Hz), 28.3 (dd, $^1J_{PC}$ = 81.4 Hz, $^2J_{PC}$ = 35.9 Hz), 14.6 (d, $^1J_{PC}$ = 18.8 Hz), 13.7 (d, $^1J_{PC}$ = 66.5 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 18.9 (d, $^3J_{PP}$ = 7.0 Hz), 6.7 (d, $^3J_{PP}$ = 6.3 Hz). Anal. Calcd for $C_{34}H_{33}BrPPd$: C, 59.19; H, 4.82. Found: C, 59.05; H, 4.94.

Pd(η^2-*m*-$MeC_6H_4CH{=}CHPMePh_2$)Br($PMePh_2$) (**5a**) was similarly obtained as yellow crystals from $Pd(dba)_2$ (130 mg, 0.225 mmol), **7a** (89.5 mg, 0.225 mmol), and $PMePh_2$ (45.1 mg, 0.225 mmol) (16%). Mp: 124–126 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 8.04–7.96, 7.78–7.45, 7.26–7.08 and 7.00–6.90 (m, 20H in total), 6.88 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.81 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 6.66 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 6.56 (s, 1H), 3.37 (ddd, $^2J_{HP}$ = 19.9 Hz, $^3J_{HH}$ = 10.7 Hz, $^3J_{HP}$ = 4.0 Hz, 1H), 3.11 (ddd, $^3J_{HP}$ = 14.3 Hz, $^3J_{HH}$ = 10.7 Hz, $^3J_{HP}$ = 8.2 Hz, 1H), 2.82 (d, $^2J_{HP}$ = 13.7 Hz, 3H), 2.11 (s, 3H), 1.51 (d, $^2J_{HP}$ = 6.2 Hz, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 144.6 (d, $^3J_{PC}$ = 12.3 Hz), 139.5 (d, $^1J_{PC}$ = 27.8 Hz), 138.2 (s), 137.0 (d, $^1J_{PC}$ = 29.4 Hz), 134.9 (d, $^3J_{PC}$ = 10.1 Hz), 133.5 (br), 132.8 (d, $^2J_{PC}$ = 14.2 Hz), 132.5 (d, $^2J_{PC}$ = 13.9 Hz), 129.9 (d, $^3J_{PC}$ = 11.2 Hz), 129.2 (s), 129.1 (d, $^3J_{PC}$ = 12.5 Hz), 128.9 (s), 128.6 (s), 128.5 (d, $^3J_{PC}$ = 9.1 Hz), 128.2 (d, $^3J_{PC}$ = 9.0 Hz), 127.4 (dd, $^1J_{PC}$ = 72.7 Hz, $^4J_{PC}$ = 9.5 Hz), 126.5 (s), 125.7 (s), 124.8 (d, $^1J_{PC}$ = 93.3 Hz), 122.6 (s), 59.8 (d, $^2J_{PC}$ = 4.9 Hz), 28.2 (dd, $^1J_{PC}$ = 81.5 Hz, $^2J_{PC}$ = 35.5 Hz), 21.5 (s), 14.6 (d, $^1J_{PC}$ = 18.7 Hz), 13.7 (d, $^1J_{PC}$ = 66.3 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 18.8 (d, $^3J_{PP}$ = 7.5 Hz), 6.7 (d, $^3J_{PP}$ = 6.2 Hz). Anal. Calcd for $C_{35}H_{35}BrP_2Pd$: C, 59.72; H, 5.01. Found: C, 59.44; H, 5.00.

Catalytic Reactions. To a 10 mL Schlenk tube containing $PhB(OH)_2$ (48.8 mg, 0.400 mmol), $Pd(PPh_3)_4$ (6.9 mg, 6.0 μmol), and hexamethylbenzene (32.5 mg, 0.200 mmol; internal standard) were added successively toluene (2.0 mL), an aqueous solution of potassium carbonate (3.0 M, 0.40 mL, 1.2 mmol), and **1** (73.2 mg, 0.400 mmol). The mixture was stirred at 80 °C for 1 h. The coupling products were identified by GC-MS using authentic samples and analyzed quantitatively by GLC.

Kinetic Experiments. A typical procedure is as follows. The compounds (*E*)-**3** (20.7 mg, 0.030 mmol), (*E*)-**1** (110 mg, 0.60 mmol), and 1,3,5-trimethoxybenzene (2.5 mg, 0.015 mmol; internal standard) were placed in an NMR sample tube and dissolved in C_6D_6/CD_2Cl_2 (5:1 v/v) (total 0.6 mL) at room temperature under a nitrogen atmosphere. The sample tube was capped with a rubber

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septum and placed in an NMR probe controlled to 50.0 ± 0.1 °C. The reaction was followed at intervals by ^{1}H NMR spectroscopy using the following marker signals: (*E*)-**3** (δ 1.98, PMe), **4** (δ 2.08, PMe), **5** (δ 2.55, 1.64, PMe), **6** (δ 2.14, PMe), **7** (δ 2.73, PMe), (*E*,*E*)-**2** (δ 6.51, vinylic H), (*E*,*Z*)-**2** (δ 6.31, vinylic H), 1,3,5-trimethoxybenzene (δ 6.14, Ar). ^{31}P{^{1}H} NMR spectrum measured after completion of the reaction exhibited three singlets assignable to **4** (δ 5.4), **6** (δ 15.2), and **7** (δ 19.3).

Reaction of *trans*-$PdBr_2(PPh_3)_2$ (4a) with $PhB(OH)_2$. To a 10 mL Schlenk tube containing **4a** (79.1 mg, 0.100 mmol), $PhB(OH)_2$ (36.6 mg, 0.300 mmol), and hexamethylbenzene (16.2 mg, 0.100 mmol; internal standard) were added successively toluene (1.0 mL) and an aqueous solution of potassium carbonate (3.0 M, 0.30 mL, 0.90 mmol). The mixture was stirred at 50 °C for 10 min and analyzed by GC-MS and GLC, showing the formation of biphenyl in quantitative yield. The reaction of **4** (*trans*/*cis* = 93/7) was similarly conducted.

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