Synthesis and Photochemical Properties of Poly(phenylenevinylene)s with Highly Regulated Structures

Masayuki Wakioka

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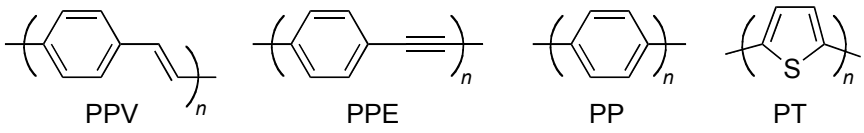
Contents

General Introduction

Background

Photo-induced Insolubilization of PPVs. π-Conjugated polymers such as poly(phenylenevinylene)s (PPVs), poly(phenyleneethynylene)s (PPEs), poly(phenylene)s (PPs), and poly(thienylene)s (PTs) have been studied extensively as organic semiconductive materials because of their desirable electronic, optical, and mechanical properties (Chart 1).[1,2] These polymers have found wide application in electronic and optoelectronic devices including light-emitting diodes (LEDs), photovoltaic cells, plastic lasers, and field-effect transistors (FETs). It has been recognized that π-conjugated polymers are advantageous over small organic molecules as well as inorganic compounds in terms of accessibility and flexibility of thin films. Accordingly, the polymers must be soluble so as to fabricate devices using easy and low-cost techniques based on wet processes. However, π-conjugated polymers often have a rigid framework and are hardly soluble in common organic solvents. Therefore, considerable efforts have been devoted to improving the solubility and processability. The incorporation of relatively long and flexible side chains such as alkyl and alkoxy groups onto the polymer backbone is a common method to prepare soluble polymers.

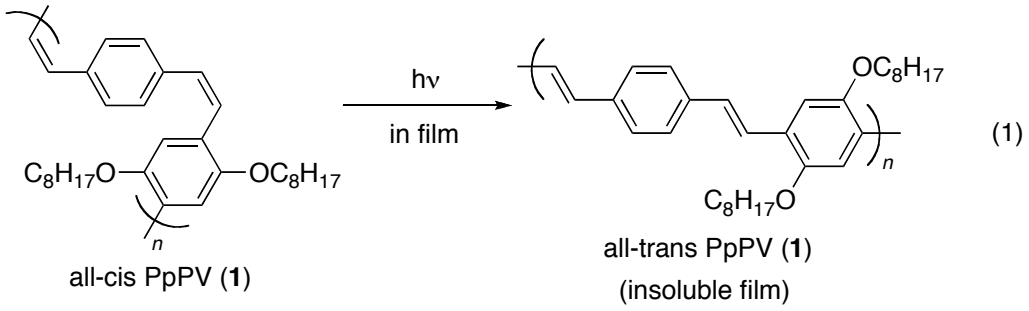
Chart 1



On the other hand, the solubility is often obstructive to the application of π-conjugated polymers. Since it is difficult to gain high device performance with a single component, several kinds of polymers are commonly combined in layers by wet processes. It has been known that the establishment of well-defined interfacial boundary of thin films is of particular importance to achieve high performance of multilayered devices.[3] Several approaches to

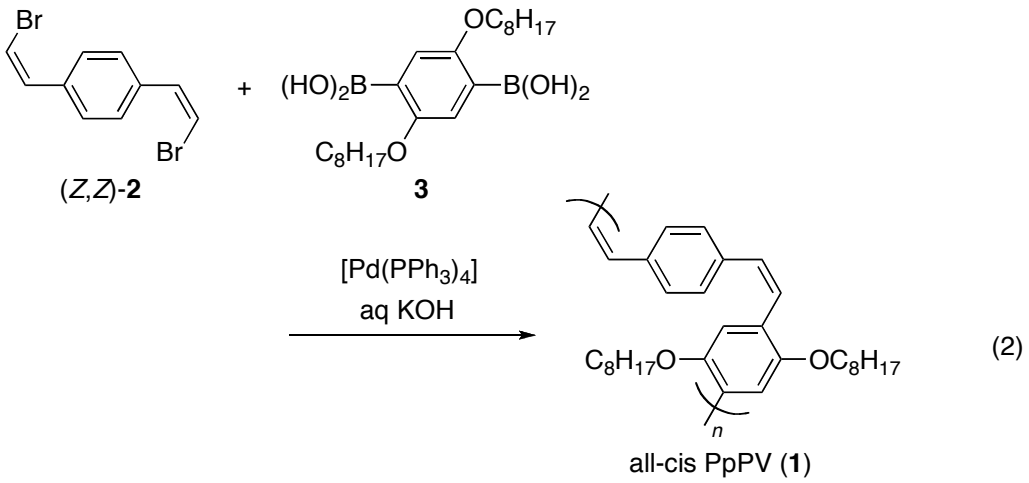
insolubilizing thin films have been developed to avoid the mixing of polymer layers within the interface. One is the selection of an appropriate solvent for each step,[4,5] and the other is the use of the polymers containing photo- or thermal-cross-linkable functional groups.[6–10] However, in any cases, the design and synthesis of appropriate polymers are not so easy task, and therefore more simple and efficient ways of insolubilizing films are desirable.

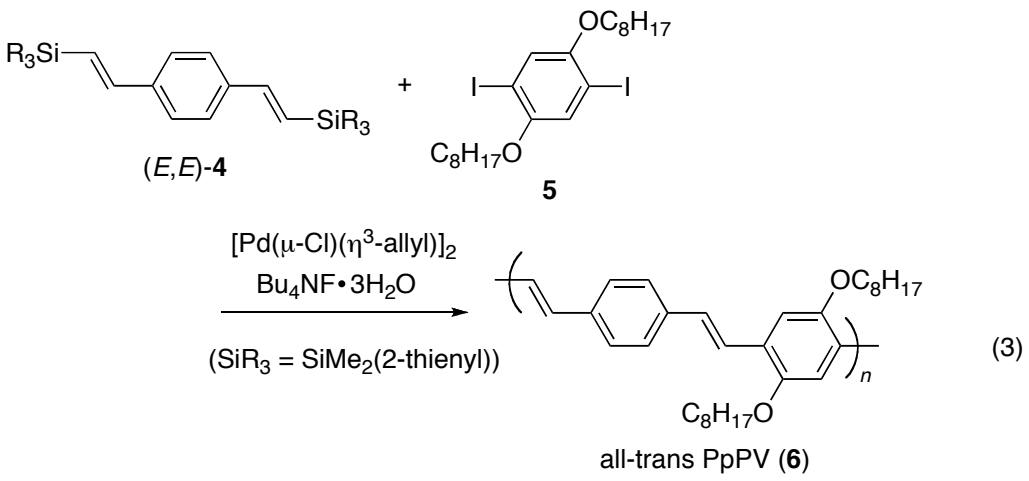
The author's group has recently found that PPVs bear very interesting properties when the vinylene linkages are entirely regulated to cis geometry.[11–13] Thus, reflecting the all-cis configuration with a zigzag structure, all-cis poly(*p*-phenylenevinylene)s (PpPVs) (**1**, eq 1) are highly soluble in common organic solvents, and exhibit excellent film-forming properties to provide highly amorphous films.[13] Furthermore, the resulting films are insolubilized under UV-irradiation, along with cis-to-trans isomerization of PpPVs. The photo-induced insolubilization has been successfully applied to direct microscale patterning of PpPVs onto quartz substrates.[11]



(1)

This phenomenon is unique to all-cis PpPVs (**1**) prepared by Suzuki–Miyaura-type polycondensation[14] of (*Z*,*Z*)-1,4-bis(2-bromoethenyl)benzene (**2**) and 2,5-dioctyloxy-1,4-benzenediboronic acid (**3**) (eq 2).[12,13] For example, all-trans isomers (**6**) independently prepared by Hiyama-type polycondensation[15] of (*E*,*E*)-1,4-bis(2-silylethenyl)benzene (**4**) and 2,5-dioctyloxy-1,4-diiodobenzene (**5**) (eq 3)[16] and poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) as a commercial product are scarcely insolubilized by UV-irradiation.



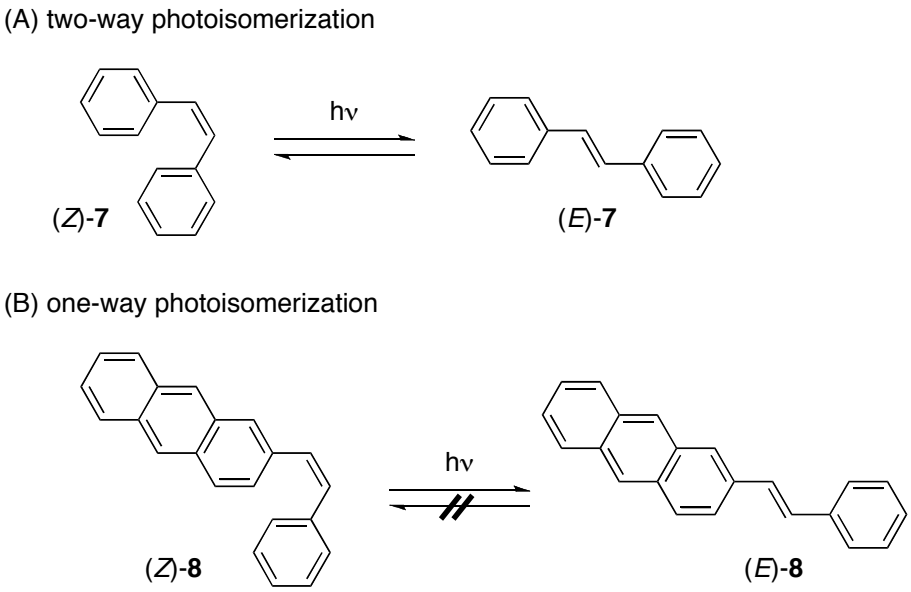


Since the above method of insolubilizing thin films is extremely simple, and possibly applied to other π-conjugated polymers, the author has been interested in elucidation of the factors governing the insolubilization phenomenon. Although photoisomerization appears to serve as a key factor, there is a possibility that several structural features characteristic of all-cis PPVs cause the insolubilization synergistically.

One-way Photoisomerization of PPVs. Alkenes are generally converted to a mixture of cis and trans isomers in the photostationary state, as typically documented for stilbene (**7**) (Scheme 1A).[17] This mutual conversion process is referred to as "two-way photoisomerization". On the other hand, some kinds of alkene with an extended π-conjugated system undergo "one-way photoisomerization", solely from cis to trans isomers, through a

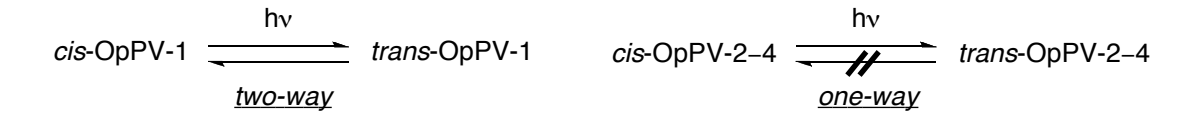
quantum chain process involving triplet excited states (Scheme 1B). 1-(2-Anthryl)-2-phenylethene (**8**) is among the representative examples. All-cis PpPVs follow the same isomerization process, as evidenced by the studies using all-cis and all-trans oligo(*p*-phenylvinylene)s (OpPVs) as well-defined models of PpPVs (Scheme 2).[18] It has been found that the isomerization mechanism changes from two-way to one-way, with extension of the π-conjugation lengths from OpPV-1 to OpPV-2.

Scheme 1



Terminal Structures of All-cis PPVs. Besides the all-cis configuration, PpPVs (**1**) prepared by Suzuki–Miyaura-type polycondensation have a characteristic structural feature; i.e., they are mainly composed of the polymer bearing 4-(2-bromoethenyl)phenyl and 2,5-dioctyloxyphenyl group at each terminus (**1x**, Chart 2).[11,12] Indeed, **1x** reacts with 2,5-dioctyloxybenzeneboronic acid in the presence of a palladium catalyst to give **1y** bearing 2,5-dioctyloxyphenyl groups at both ends.[12] Since the terminal groups of all-cis **1x** are very probably preserved in all-trans PpPV formed by photoisomerization, but not in all-trans PpPV (**6**) prepared by Hiyama-type polycondensation (eq 3), there is a possibility that the unique terminal structure of **1x** serves as a promoter of the photo-induced insolubilization.

Scheme 2



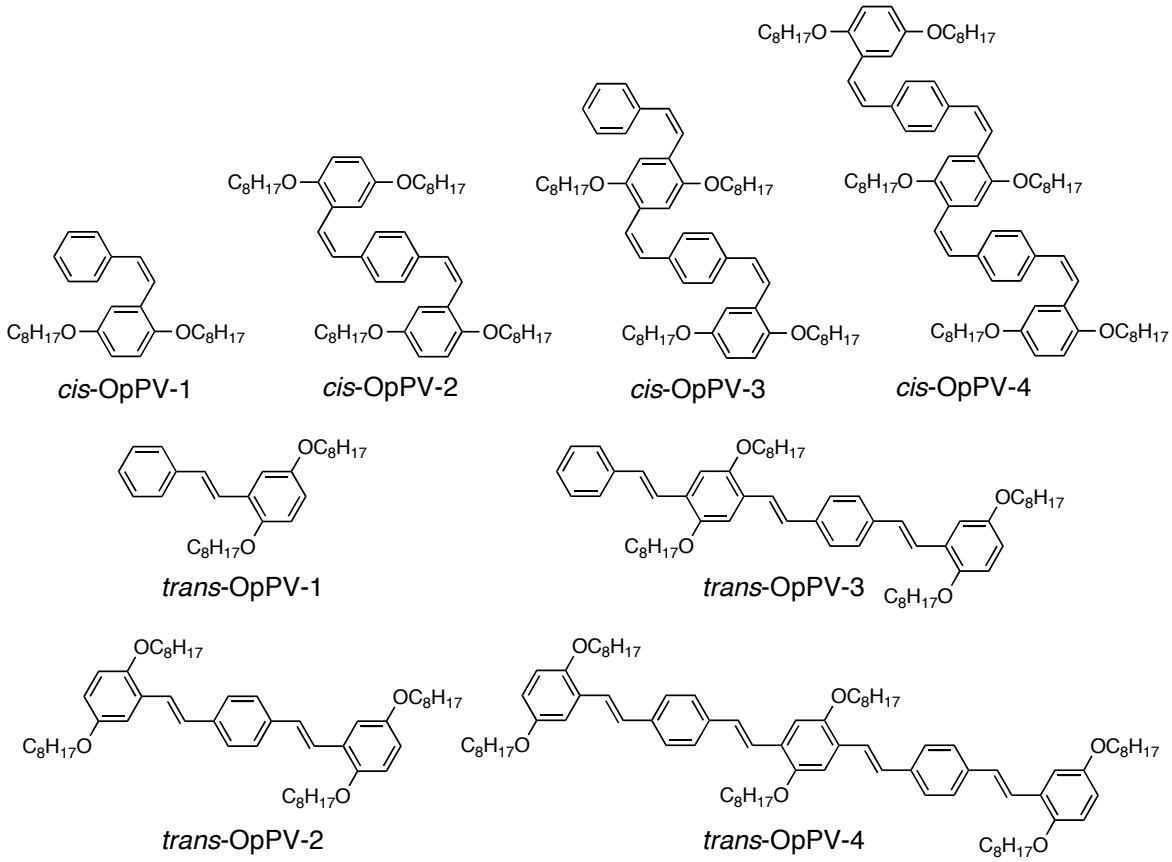
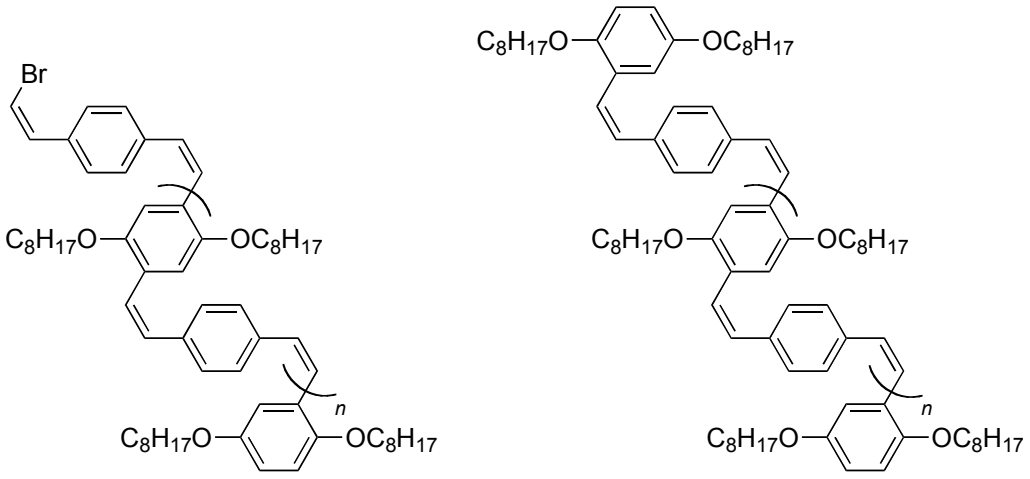


Chart 2



On the Factors for Photo-induced Insolubilization. Taking the above observations into account, the author set about the following subjects.

(1) Effect of all-cis and all-trans configurations on photo-induced insolubilization.

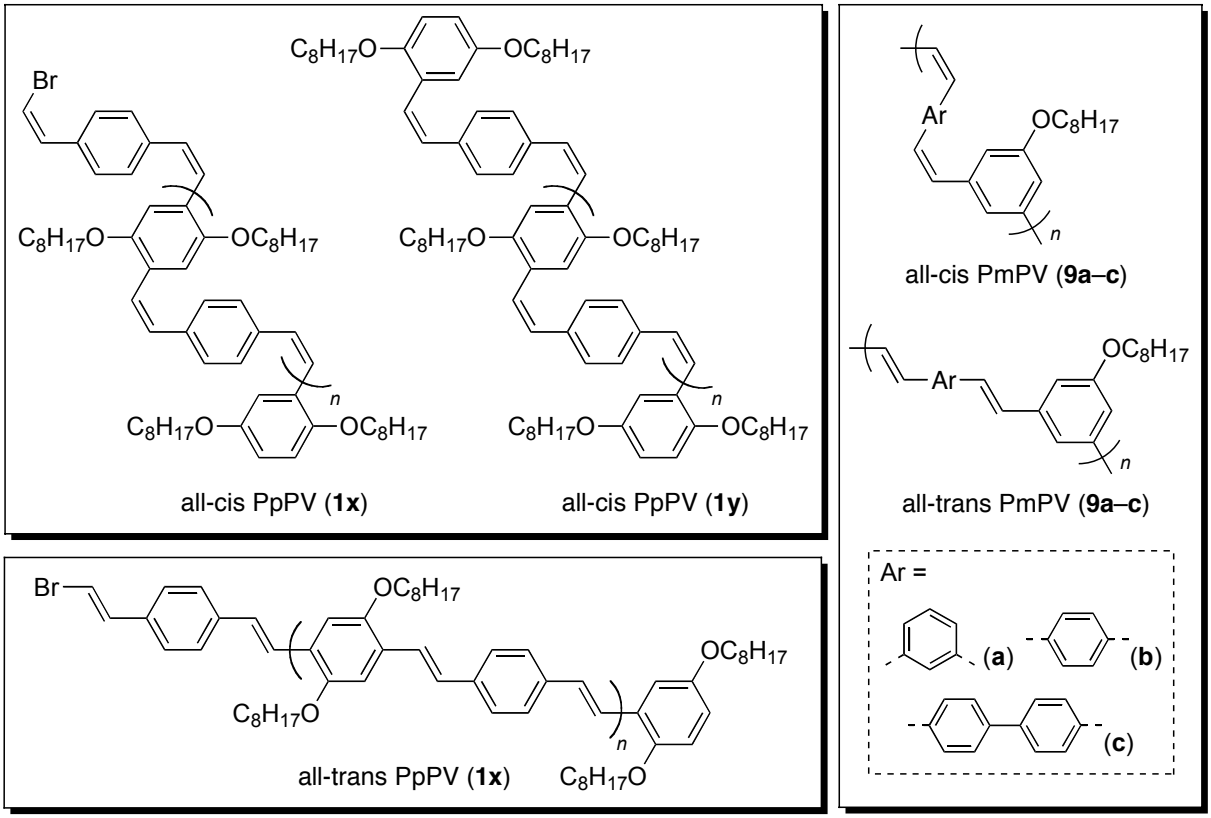
(2) Effect of terminal structures on photo-induced insolubilization.

(3) Effect of molecular weight on photo-induced insolubilization.

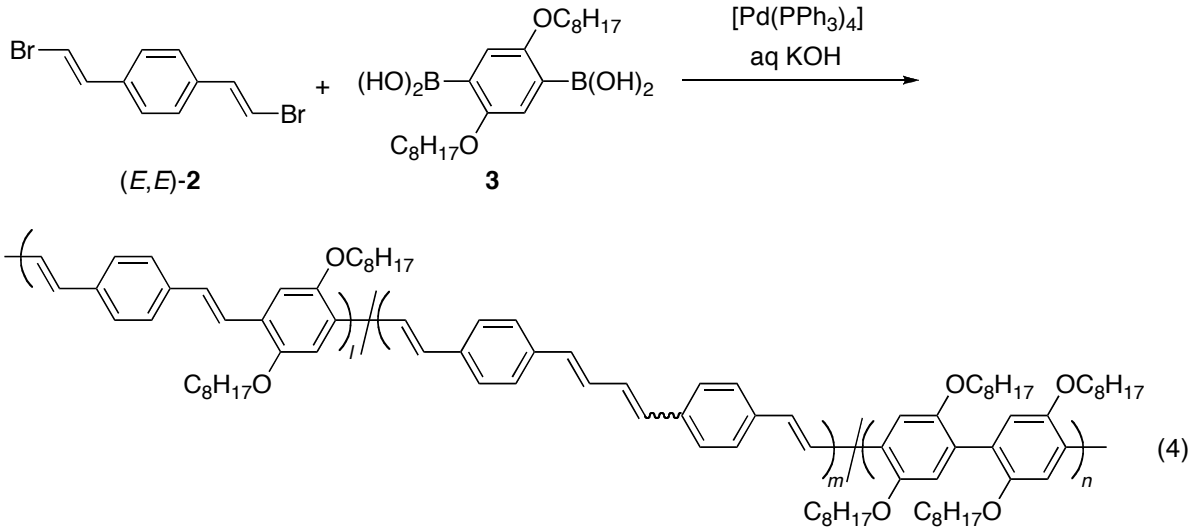
(4) Effect of π-conjugation length on photoisomerization in polymer systems.

To deal with these subjects, the following sets of PPVs with all-cis and all-trans configurations have been required in a range of molecular weights, respectively (Chart 3). Among them, all-cis PpPVs (**1x** and **1y**) have already been synthesized, whereas all-trans PpPVs (**1x**) bearing the same terminal groups as all-cis **1x** and all-cis and all-trans poly(*m*-phenylenevinylene)s (PmPVs, **9a**–**c**) bearing relatively short effective π-conjugation lengths interrupted by *m*-phenylene units[19] have not been obtained. The all-cis and all-trans

Chart 3



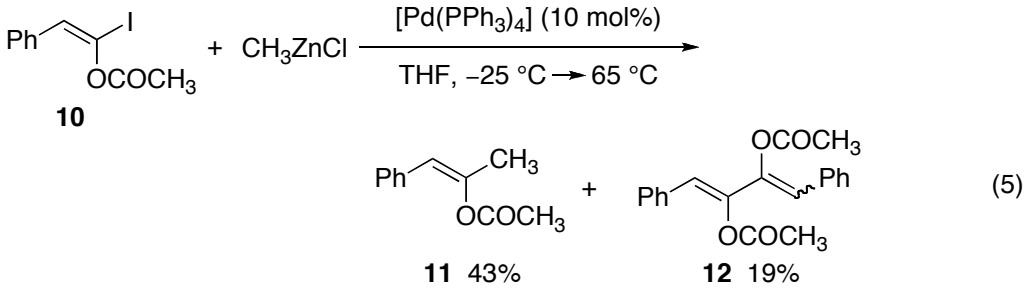
isomers of **9a**–**c** may be prepared similarly to all-cis **1** and all-trans **6**, respectively.[12,16] On the other hand, although all-trans **1x** having 4-(2-bromoethenyl)phenyl and 2,5-dioctyloxyphenyl groups at each terminus needs to be prepared by Suzuki–Miyaura-type polycondensation, the previous attempts in this group have been unsuccessful due to contamination of the polymer chain with butadiene and biaryl units (eq 4).[20]



(4)

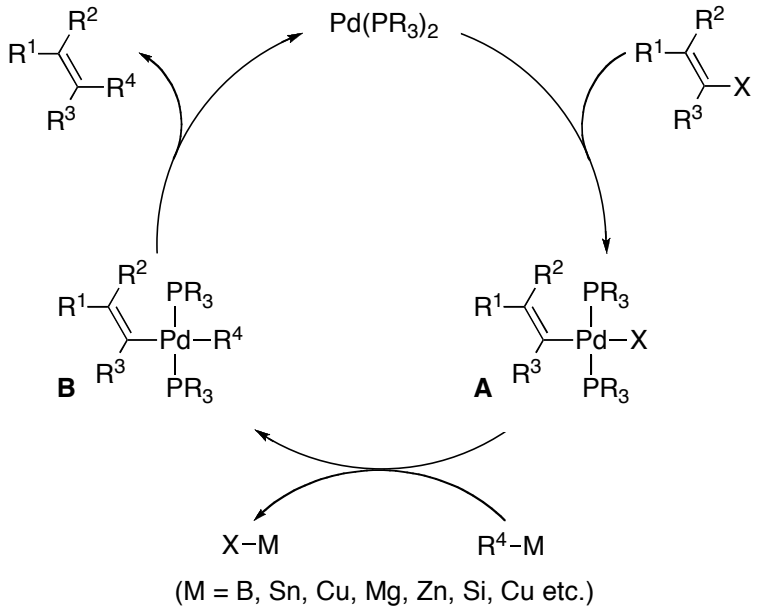
These structural defects are due to homo-coupling processes. Because structural defects once generated in the polymer chain are unable to be removed by purification, the establishment of a highly selective catalytic condition has been essential to achieve the synthesis of all-trans PpPVs.

Cross-Coupling vs. Homo-Coupling Reactions. Cross-coupling reactions of alkenyl halides with organometallic reagents are useful means of regio- and stereo-selective synthesis of alkenes.[21] However, they often involve undesirable homo-coupling reactions.[22] For example, Negishi coupling of alkenyl iodide (**10**) with methylzinc chloride catalyzed by $[Pd(PPh_3)_4]$ forms butadiene **12** as the homo-coupling product, together with **11** as the cross-coupling product (eq 5).[22e]



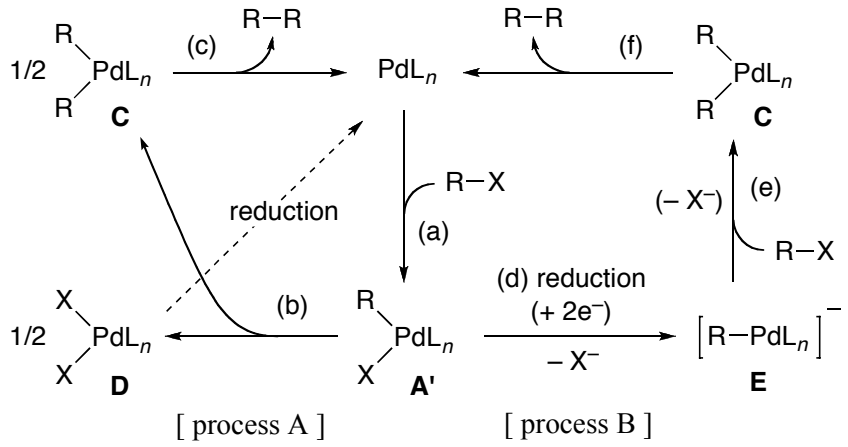
Scheme 3 illustrates the catalytic cycle of cross-coupling generally accepted. First, a low-valent palladium species $[Pd(PR_3)_2]$ undergoes oxidative addition of alkenyl halides to form an alkenylpalladium intermediate **A**. Transmetalation of **A** with organometallic compounds affords intermediate **B**, which reductively eliminates cross-coupling products, along with regeneration of $[Pd(PR_3)_2]$. Mechanistic studies using experimental and computational techniques have shown that transmetalation serves as the rate-determining step in many catalytic systems.[21] Consequently, it is likely that the homo-coupling reaction proceeds from **A** as a common intermediate.

Scheme 3. Proposed Mechanism of Cross-Coupling Reactions of Alkenyl Halides



In contrast to the extensive studies of cross-coupling reactions, the mechanism of homo-coupling reactions has been little explored.[23–25] Scheme 4 illustrates a schematic view of homo-coupling processes so far reported. Organopalladium intermediate **A'**, formed by oxidative addition of organic halide (R–X) to a low-valent palladium species (step a), possibly undergoes two reaction processes (A and B). Process A involves disproportionation of **A'** to give diorgano (**C**) and dihalogeno (**D**) complexes (step b), and **C** subsequently undergoes reductive elimination of homo-coupling product (R–R) (step c).[24] On the other hand, process **B** involves oxidative addition of R–X to an anionic species (**E**), generated by chemical or electrochemical reduction of **A'** (step d → step e). The resulting diorganopalladium **C** reductively eliminates R–R (step f).[25] The reaction mechanism possibly depends on catalytic conditions including the sorts of organic halides and supporting ligands. For example, process A has been proposed for the homo-coupling reaction of aryl halides catalyzed by a Pd/bipy complex,[24] while process B for the reaction of aryl triflates promoted by a Pd/PPh_3 catalyst.[25] In any case, however, the mechanistic information is extremely limited, and direct information about the present catalytic systems of all-trans PpPV synthesis is desirable.

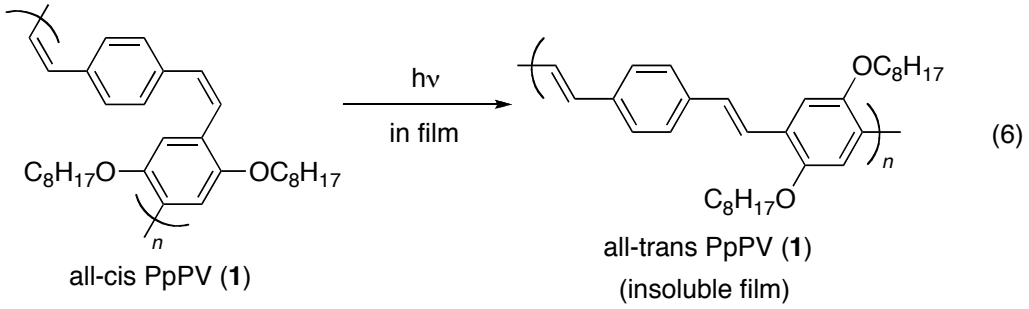
Scheme 4



Outline of the Thesis

To elucidate the unique photochemical properties of all-cis PpPVs, the author deals with the subjects (1)–(4) set in the previous section by examining the following topics.

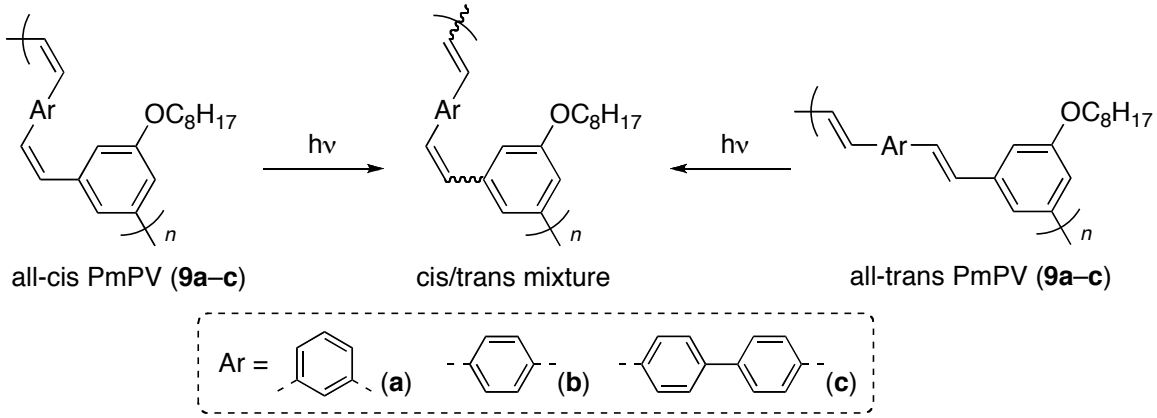
Chapter 1 deals with photo-induced insolubilization of all-cis PpPVs (**1**) (subjects (2) and (3)) (eq 6). To investigate the effects of terminal structures and molecular weights on photo-induced insolubilization, the author prepared all-cis **1x** and **1y** (Chart 3) with a range of molecular weights, and examined their performance by a quantitative method using UV-vis absorption spectroscopy. It has been found that the performance of all-cis PpPVs on photo-induced insolubilization is significantly affected by terminal structures as well as molecular weights; namely, 2-bromoethenyl groups at the polymer end facilitates the insolubilization to a notable extent.



(6)

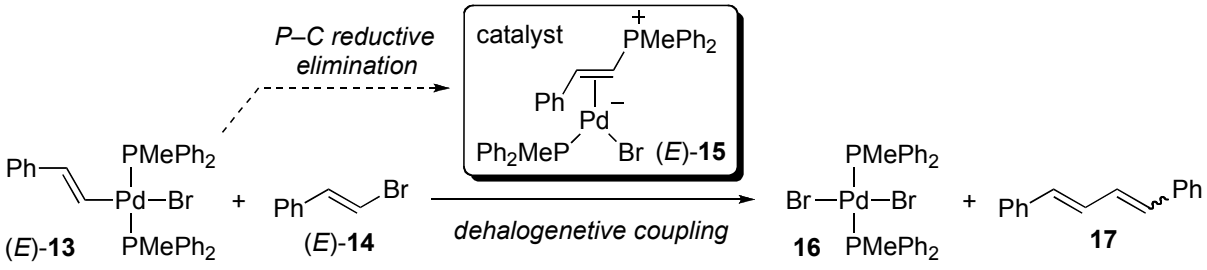
Chapter 2 deals with photoisomerization of PPVs (subject (4)). To examine the effects of π-conjugation lengths on photoisomerization, all-cis and all-trans PmPVs (**9a**–**c**) having relatively short effective π-conjugation lengths (Chart 3) were synthesized in almost perfect stereoregularities by Suzuki–Miyaura-type and Hiyama-type polycondensation, respectively. It has been found that the resulting PmPVs undergo two-way photoisomerization both in solution and thin films, in contrast to PpPVs, which undergo one-way photoisomerization (Scheme 5). Thus, the dependence of the photoisomerization mechanism on π-conjugation lengths has been clarified for the first time in polymer systems.

Scheme 5



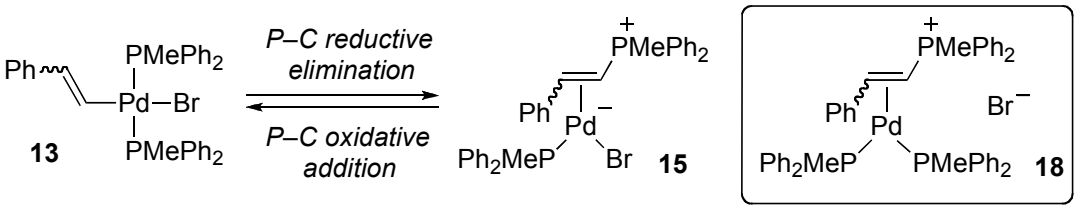
To examine whether the all-cis configuration of PpPVs is essential or not on photo-induced insolubilization (subject (1)), all-trans PpPVs bearing a 2-bromoethenyl group (all-trans **1x**, Chart 3) has been required. For ensuring the highly selective synthesis of all-trans PpPVs without structural defects, the author has examined in Chapter 3 to clarify the mechanism of homo-coupling giving 1,4-diphenylbutadiene from styryl bromide. Thus, the isolated *trans*-[Pd(CH=CHPh)Br($PMePh_2$)$_2$] (**13**) as a model of presumed intermediate was treated with (*E*)-styryl bromide (**14**) in a stoichiometric system, and the reaction was investigated in detail by NMR spectroscopy and kinetic techniques. The study has revealed that [Pd(η^2-(*E*)-PhCH=CHP$MePh_2$)Br($PMePh_2$)] (**15**) formed by P–C reductive elimination from (*E*)-**13** catalyzes the conversion of (*E*)-**13** and (*E*)-**14** into *trans*-[$PdBr_2$($PMePh_2$)$_2$] (**16**) and 1,4-diphenylbutadiene (**17**) (Scheme 6).

Scheme 6



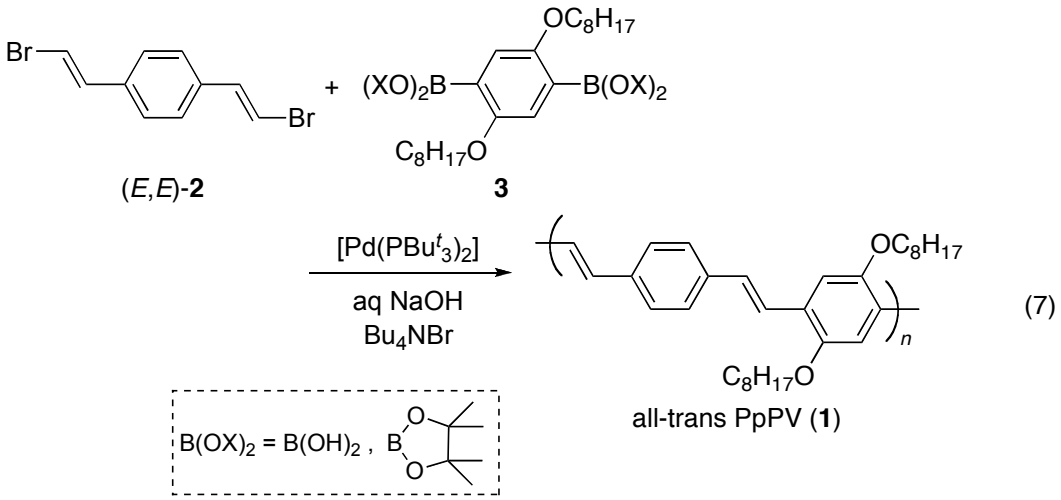
In this connection, Chapter 4 deals with the mechanism of P–C reductive elimination from *trans*-[Pd(CH=CHPh)Br($PMePh_2$)$_2$] (**13**) to afford [Pd(η^2-PhCH=CHP$MePh_2$)Br-($PMePh_2$)] (**15**) and [Pd(η^2-PhCH=CHP$MePh_2$)($PMePh_2$)$_2$]Br (**18**) (Scheme 7). It has been shown that the P–C reductive elimination is strongly dependent on E/Z configurations of styryl ligand. Thus, the (*E*)-isomer of **13** easily undergoes P–C reductive elimination. On the other hand, while the (*Z*)-isomer of **13** is inactive toward P–C reductive elimination, the (*Z*)-styrylphosphonium complex (*Z*)-**15** undergoes P–C oxidative addition to give (*Z*)-**13**. Kinetic examinations clearly demonstrate that the P–C reductive elimination from (*E*)-**13** proceeds via either a dissociative or an associative path, depending on the amount of free $PMePh_2$ in the system.

Scheme 7.



Chapter 5 describes highly selective synthesis of all-trans PpPVs (**1x**) via Suzuki–Miyaura-type polycondensation (eq 7). The catalytic conditions were investigated for a model reaction of (*E*)-styryl bromide with 2,5-dioctyloxybenzeneboronic acid, taking the mechanistic information gained in Chapters 3 and 4 into consideration. The combination of [Pd(PBu^t_3)$_2$], aqueous NaOH, and Bu_4NBr was found to be particularly effective for cross-coupling, and thereby all-trans PpPVs without structural defects were successfully prepared by polycondensation of (*E*,*E*)-**2** with **3**. A detailed NMR analysis of the resulting all-trans PpPVs revealed the same terminal structures as found in all-cis PpPVs. The polymers did undergo photo-induced insolubilization in thin films, but their performance was

much lower than that of all-cis isomers. Hence, the importance of all-cis configuration of PpPVs for the photo-induced insolubilization has been evidenced.



(7)

References and Notes

(1) (a) Richardson, T. H., Eds. *Functional Organic and Polymeric Materials*; John Wiley & Sons: Chichester, England, 2000. (b) Sheats, J. R.; Barbara, P. F., Eds. *Molecular Materials in Electronic and Optoelectronic Devices. Acc. Chem. Res.* **1999**, *32*, 191–276.

(2) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402–428. (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121–128. (c) Scherf, U. *Top. Curr. Chem.* **1999**, *201*, 163–222. (d) Akcelrud, L. *Prog. Polym. Sci.* **2003**, *28*, 875–962.

(3) Veinot, J. G. C.; Marks, T. J. *Acc. Chem. Res.* **2005**, *38*, 632–643.

(4) (a) Yang, Y.; Westerweele, E.; Zhang, C.; Smith, P.; Heeter, A. J. *J. Appl. Phys.* **1995**, *77*, 694–698. (b) Cao, Y.; Yu, G.; Zhang, C.; Menon, R.; Heeger, A. J. *Synth. Met.* **1997**, *87*, 171–174. (c) Gong, X.; Wang, S.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv.*

Mater. **2005**, *17*, 2053–2058. (d) Shi, W.; Fan, S.; Huang, F.; Yang, W.; Liu, R.; Cao, Y. *J. Mater. Chem.* **2006**, *16*, 2387–2394.

(5) (a) Huang, F.; Wu, H.; Wang, D.; Yang, W.; Cao, Y. *Chem. Mater.* **2004**, *16*, 708–716. (b) Wu, H.; Huang, F.; Mo, Y.; Yang, W.; Wang, D.; Peng, J.; Cao, Y. *Adv. Mater.* **2004**, *16*, 1826–1830. (c) Huang, F.; Hou, L.; Wu, H.; Wang, X.; Shen, H.; Cao, W.; Yang, W.; Cao, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9845–9853. (d) Ma, W.; Iyer, P. K.; Gong, X.; Liu, B.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv. Mater.* **2005**, *17*, 274–277. (e) Huang, F.; Hou, L.; Shen, H.; Jiang, J.; Wang, F.; Zhen, H.; Cao, Y. *J. Mater. Chem.* **2005**, *15*, 2499–2507. (f) Huang, F.; Niu, Y.-H.; Zhang, Y.; Ka, J.-W.; Liu, M. S.; Jen, A. K.-Y. *Adv. Mater.* **2007**, *19*, 2010–2014.

(6) Badarau, C.; Wang, Z. Y. *Macromolecules* **2004**, *37*, 147–153.

(7) (a) Bacher, A.; Erdelen, C. H.; Paulus, W.; Ringsdorf, H.; Schmidt, H.-W.; Schuhmacher, P. *Macromolecules* **1999**, *32*, 4551–4557. (b) Kim, K.-H.; Jang, S.; Harris, F. W. *Macromolecules* **2001**, *34*, 8925–8933. (c) Zhang, Y.-D.; Hreha, R. D.; Jabbour, G. E.; Kippelen, B.; Peyghambarian, N.; Marder, S. R. *J. Mater. Chem.* **2002**, *12*, 1703–1708. (d) Hua, J. L.; Lam, J. W. Y.; Dong, H.; Wu, L.; Wong, K. S.; Tang, B. Z. *Polymer*, **2006**, *47*, 18–22. (e) Wu, L.; Tomg, W. Y. Y.; Zhong, Y.; Wong, K. S.; Hua, J.; Häußler, M; Lam, J. W. Y.; Tang, B. Z. *Appl. Phys. Lett.* **2006**, *89*, 191109.

(8) (a) Chen, J. P.; Klaerner, G.; Lee, J.-I.; Markiewicz, D.; Lee, V. Y.; Miller, R. D.; Scott, J. C. *Synth. Met.* **1999**, *107*, 129–135. (b) Klaerner, G.; Lee, J.-I.; Lee, V. Y.; Chan, E.; Chen, J.-P.; Nelson, A.; Markiewicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800–1805. (c) Sun, H.; Liu, Z.; Hu, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2124–2129. (d) Paul, G. K.; Mwaura, J.; Argun, A. A.; Taranekar, P.; Reynolds, J. R. *Macromolecules* **2006**, *39*, 7789–7792.

(9) (a) Bayerl, M. S.; Braig, T.; Nuyken, O.; Müller, D. C.; Groß, M.; Meerholz, K. *Macromol. Rapid Commun.* **1999**, *20*, 224–228. (b) Müller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Ruudati, P.; Frohne, H.; Nuyken, O.;

Becker, H.; Meerholz, K. *Nature* **2003**, *421*, 829–833. (c) Bacher, E.; Jungermann, S.; Rojahn, M.; Wiederhirn, V.; Nuyken, O. *Macromol. Rapid Commun.* **2004**, *25*, 1191–1196. (d) Bacher, E.; Bayerl, M.; Rudati, P.; Reckefuss, N.; Müller, C. D.; Meerholz, K.; Nuyken, O. *Macromolecules* **2005**, *38*, 1640–1647. (e) Jungermannm, S.; Riegel, N.; Müller, D.; Meerholz, K.; Nuyken, O. *Macromolecules* **2006**, *39*, 8911–8919. (f) Tang, D.-F.; Wen, G.-A.; Qi, X.-Y.; Wang, H.-Y.; Peng, B.; Wei, W.; Huang, W. *Polymer* **2007**, *48*, 4412–4418.

(10) Feng, K.; Tsushima, M.; Matsumoto, T.; Kurosaki, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 685–693.

(11) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Umeda, K.; Akamatsu, K.; Tsuruoka, T.; Nawafune, H.; Ozawa, F. *J. Am. Chem. Soc.* **2005**, *127*, 4350–4353.

(12) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Fukuse, Y.; Wakioka, M.; Ozawa, F. *Macromolecules* **2006**, *39*, 2039–2048.

(13) Katayama, H.; Ozawa, F.; Matsumiya, Y.; Watanabe, H. *Polym. J.* **2006**, *38*, 184–189.

(14) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483. (b) Miyaura N. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A.; Diederich, F. Eds; WILEY-VCH, Weinheim, Germany, 2004; Chapter 2.

(15) (a) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845–853. (b) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471–1478. (c) Hiyama T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F.; Stang, P. J. Eds; WILEY-VCH, Weinheim, Germany, 1998; Chapter 10. (d) Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A.; Diederich, F. Eds; WILEY-VCH, Weinheim, Germany, 2004; Chapter 4.

(16) Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet. Chem.* **2003**, *676*, 49–54.

(17) (a) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415–436. (b) Meier, H. *Angew. Chem., Int. Ed. Eng.* **1992**, *31*, 1399–1420. (c) Arai, T.; Tokumaru, K. *Chem. Rev.* **1993**, *93*, 23–39.

(18) (a) Katayama, H.; Nagao, M.; Ozawa, F.; Ikegami, M.; Arai, T. *J. Org. Chem.* **2006**, *71*, 2699–2705. (b) Ikegami, M.; Nagao, M.; Katayama, H.; Ozawa, F.; Arai, T. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1833–1835.

(19) (a) Doi, S.; Osada, T.; Tsuchida, Y.; Noguchi, T.; Ohnishi, T. *Synth. Met.* **1997**, *85*, 1281–1282. (b) Davey, A. P.; Drury, A.; Maier, S.; Byrne, H. J.; Blau, W. J. *Synth. Met.* **1999**, *103*, 2478–2479. (c) Ahn, T.; Jang, M. S.; Shim, H.-K.; Hwang, D.-H.; Zyung, T. *Macromolecules* **1999**, 32, 3279–3285. (d) Pang, Y.; Li, J.; Hu, B.; Karasz, F. E. *Macromolecules* **1999**, *32*, 3946–3950. (e) Schlick, H.; Stelzer, F.; Tasch, S.; Leising, G. *J. Mol. Cat. A: Chem.* **2000**, *160*, 71–84. (f) Schlick, H.; Stelzer, F.; Meghdadi, F.; Leising, G. *Synth. Met.* **2001**, *119*, 529–530. (g) Liao, L.; Pang, Y.; Ding, L.; Karasz, F. E. *Macromolecules* **2001**, *34*, 6756–6760. (h) Liao, L.; Pang, Y.; Ding, L.; Karasz, F. E. *Macromolecules* **2001**, *34*, 7300–7305. (i) Drury, A.; Maier, S.; Ruether, M.; Blau, W. J. *J. Mater. Chem.* **2003**, *13*, 485–490.

(20) Nishimura, T.; Nagao, M.; Katayama, H.; Ozawa, F. unpublished results.

(21) de Meijere, A.; Diederich, F. Eds. *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; WILEY-VCH, Weinheim, Germany, 2004.

(22) (a) Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Organomet. Chem.* **1987**, *334*, 181–194. (b) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813–817. (c) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393–2401. (d) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 4909–4914. (e) Rossi, R.; Carpita, A.; Cossi, P. *Tetrahedron* **1992**, *48*, 8801–8824. (f) Wang, Z.; Wnuk, S. F. *J. Org. Chem.* **2005**, *70*, 3281–3284. (g) Andrei, D.; Wnuk, S. F. *J. Org. Chem.* **2006**, *71*, 405–408. (h) Barluenga, J.; Moriel, P.; Aznar, F.; Valdés, C. *Org. Lett.* **2007**, *9*, 275–278. (i) Batsanov, A. S.; Knowles, J. P.; Whiting, A. *J. Org. Chem.* **2007**, *72*, 2525–2532.

(23) Osakada, K. In *Current Methods in Inorganic Chemistry*; Yamamoto, A., Kurosawa, H., Eds.; Elsevier: Amsterdam, 2003; Vol. 3, Chapter 5.

(24) (a) Yamamoto, T.; Wakabayashi, S.; Osakada, K. *J. Organomet. Chem.* **1992**, *428*, 223–237. (b) Yagyu, T.; Hamada, M.; Osakada, K.; Yamamoto, T. *Organometallics* **2001**, *20*, 1087–1101. (c) Suzaki, Y.; Osakada, K. *Organometallics* **2003**, *22*, 2193–2195. (d) Suzaki, Y.; Osakada, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 139–145. (e) Suzaki, Y.; Yagyu, T.; Osakada, K. *J. Organomet. Chem.* **2007**, *692*, 326–342.

(25) (a) Amatore, C.; Jutand, A. *Organometallics* **1988**, *7*, 2203–2214. (b) Jutand, A.; Mosleh, A. *J. Org. Chem.* **1997**, *62*, 261–274. (c) Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254–278. (d) Jutand, A. *Eur. J. Inorg. Chem.* **2003**, 2017–2040.

Chapter 1

Effects of Primary Structures on Photo-induced Insolubilization of Poly(phenylenevinylene)s in Thin Films

Abstract

All-cis poly(*p*-phenylenevinylene)s (PpPVs) prepared by Suzuki–Miyaura-type polycondensation of (*Z*,*Z*)-1,4-bis(2-bromoethenyl)benzene with 2,5-dioctyloxybenzene-1,4--diboronic acid undergo photo-induced insolubilization in thin films, along with trans-to-cis isomerization of vinylene groups to give all-trans PpPVs. This phenomenon has been investigated with two types of all-cis PpPVs having different terminal structures; one bears (*Z*)-4-(2-bromoethenyl)phenyl and 2,5-dioctyloxyphenyl group at each terminus, whereas the other has 2,5-dioctyloxyphenyl groups at both ends. The amount of all-trans PpPV remaining on a quartz substrate, after UV-irradiation on a spin-coated thin film of all-cis PpPV, followed by rinsing twice with $CHCl_3$, is clearly dependent on the molecular weight and terminal groups of the starting polymer. It has been found that (*Z*)-4-(2-bromoethenyl)phenyl group facilitates the photo-induced insolubilization to a notable extent. The insolubilized films exhibit the hole mobility (μ_{FET}) of up to 1.6×10^{-4} cm^2 V^{-1} s^{-1}.

Introduction

Recently, a great deal of effort has been devoted to the development of polymeric semiconductors, which are key components of flexible electronic devices such as organic field effective transistors (OFETs) and organic light-emitting diodes (OLEDs).[1] Poly(*p*-phenylenevinylene)s (PPVs) are among the most studied ones.[2] A distinct advantage of polymeric materials is the accessibility of thin films by solution processes such as spin-coating and dip-coating, which enable easy and low-cost fabrication of devices. Since it is difficult to gain high device performance with a single component, most of the devices are composed of multilayer structures. In this connection, several methods of insolubilizing thin films have been developed to avoid interfusion of polymer layers upon multi-coating; the establishment of well-defined interfacial boundary of thin films is an essential requirement for achieving high device performance.[3] The most extensively investigated method is the use of photo- or thermal-cross-linkable polymers.[4–14] Alternatively, soluble precursors coated onto substrates are thermally converted to insoluble polymers.[2] Although insoluble films of PPVs are generally prepared by the latter method, it has been known that the resulting polymers often involve structural defects due to incomplete reactions.[15]

The author's group has recently found that PPVs gain a very unique film-forming property when the vinylene linkages are highly regulated to cis geometry.[16] Thus, all-cis PPVs (M_n = 4700 and 5000), prepared by Suzuki–Miyaura-type polycondensation of (*Z*,*Z*)-1,4- and (*Z*,*Z*)-1,3-bis(2-bromoethenyl)benzenes with 2,5-dioctyloxy-benzene-1,4-diboronic acid, form highly amorphous films by spin-coating.[16c] Interestingly, the resulting films become insoluble in common organic solvents under UV light, along with cis-to-trans isomerization of vinylene linkages.[16a] Although one may assume that photoisomerization giving all-trans PPV with a rigid framework causes the insolubilization phenomenon, it has been found that PPV (M_n = 7200, M_w/M_n = 1.81) independently prepared in all-trans form[17] remains soluble under UV light, showing the presence of additional factors other than all-cis

configuration. Consequently, it has been considered that some primary structures unique to all-cis PPVs cause the photo-induced insolubilization.

In this Chapter, all-cis poly(*p*-phenylenevinylene)s (PpPVs) were prepared with a range of molecular weights and end-group structures, and examined their performance by a quantitative method. It has been found that the presence of a 2-bromoethenyl group at the polymer end is of significance for insolubilization to proceed efficiently under UV light. The insolubilized films exhibit the carrier mobility (μ_{FET}) of up to 1.6×10^{-4} cm^2 V^{-1} s^{-1}.

Results and Discussion

Preparation of All-cis PpPVs. As previously reported, the palladium-catalyzed polycondensation of (*Z*,*Z*)-1,4-bis(2-bromoethenyl)benzene (**1**) with 2,5-dioctyloxybenzene-1,4-diboronic acid (**2**) forms two types of all-cis PpPVs (**3** and **4**) having different terminal structures (Scheme 1).[16a] Polymer **3** bears (*Z*)-(2-bromoethenyl)phenyl and 2,5-dioctyloxyphenyl group at each terminus, whereas **4** is substituted with 2,5-dioctyloxyphenyl groups at both ends. Detailed examination of all-cis PpPV with M_n of 2400 has revealed that the catalytic polycondensation reaction produces "type I polymer" mainly composed of **3**. This product can be converted to "type II polymer" predominantly consisting of **4** by end-capping with 2,5-dioctyloxybenzeneboronic acid (**5**).[16b]

Scheme 1. Synthetic Routes to All-cis PpPVs

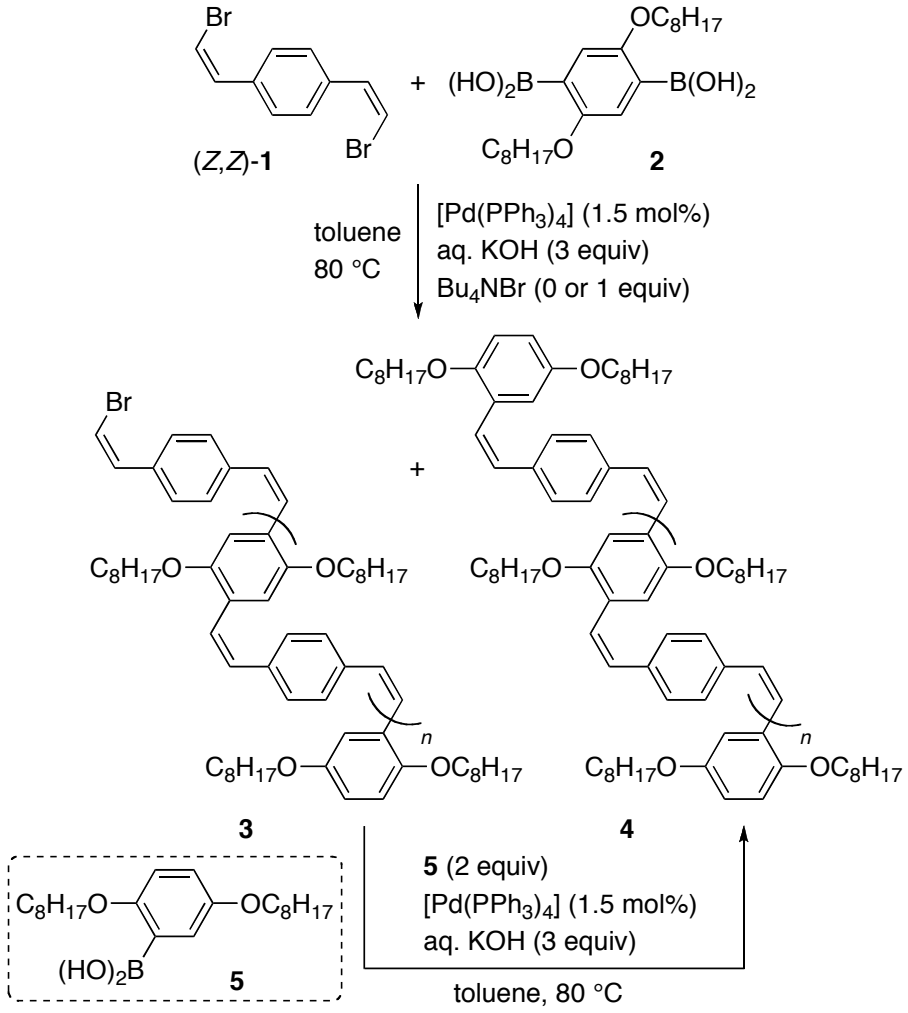


Table 1 lists the all-cis PpPVs prepared in this study. The molecular weights of type I polymers (**Ia**–**h**) vary with catalytic conditions, especially with the absence or presence of Bu_4NBr as a phase transfer catalyst.[16b] The polymers with M_n of less than 3000 are obtained in the absence of Bu_4NBr, while the molecular weight increases up to 8100 in the presence of Bu_4NBr (1 equiv). The bromine content in low molecular weight polymers (**Ib** and **Ic**) is in a 20% relative error range of the calculated values, showing the predominance of **3** in these polymers. On the other hand, the bromine content in higher molecular weight polymers (**Id**, **If**, and **Ig**) is apparently lower than the calculated values; the content of **3** is estimated to be 56–76% of the whole polymers.

Table 1. Specifications and Performance on Insolubilization of All-cis PpPVs

all-cis PpPV	M_n [a]	M_w/M_n [a]	Br (%) [b]	insolubilized PpPV (%) [c]
Ia	1800	1.39	*e*	36
Ib	2800	1.55	2.29 [2.85]	33
Ic	3500	1.55	2.63 [2.28]	59
Id	4700	2.79	1.10 [1.70]	56
Ie	4800	2.20	*e*	64
If	6600	3.14	0.68 [1.21]	85
Ig	7000	2.69	0.87 [1.14]	84
Ih	8100	3.93	*e*	89
IIa	2400	1.24	0.41 [3.33]	2
IIb [d]	5000	1.03	*e*	11
IIc [d]	7700	1.11	*e*	35

[a] Determined by GPC calibration based on polystyrene standards. [b] Determined by elemental analysis. The numbers in brackets are calculated values for pure **3** having the corresponding M_n values. [c] See text. [d] Separated from **IIa** by recycle GPC. [e] Not determined.

Type II polymer **IIa** was prepared by palladium-catalyzed polycondensation, followed by end-capping of **3** with **5**.[16b] Since the end-capping did not proceed cleanly with higher molecular weight polymers, **IIb** and **IIc** were separated from **IIa** by recycle GPC.

Photo-induced Insolubilization of All-cis PpPVs. Figure 1 illustrates the experimental procedure for photo-induced insolubilization. (i) A thin film of type I or type II polymer was prepared from a $CHCl_3$ solution (2.0 wt%) by spin-coating, and (ii) irradiated with UV light (λ = 300–400 nm, 21.0 mW cm^{-2}) for 1 h at room temperature under vacuum. (iii) The irradiated film was rinsed twice with $CHCl_3$ and dried.

Figure 2 compares the UV-vis absorption spectra of the films at steps (i)–(iii). (i) The thin film of all-cis PpPV exhibits the π–π^* transition at 388 nm. (ii) This absorption disappears upon UV-irradiation, and a strong absorption assignable to the π–π^* transition of all-trans PPV appears at 466 nm instead. (iii) The absorption remains after rinsing with $CHCl_3$, though the intensity drops to a certain extent. In the case of **Ig** as a type I polymer, 84% of the intensity of spectrum (ii) was preserved in spectrum (iii). This value corresponds

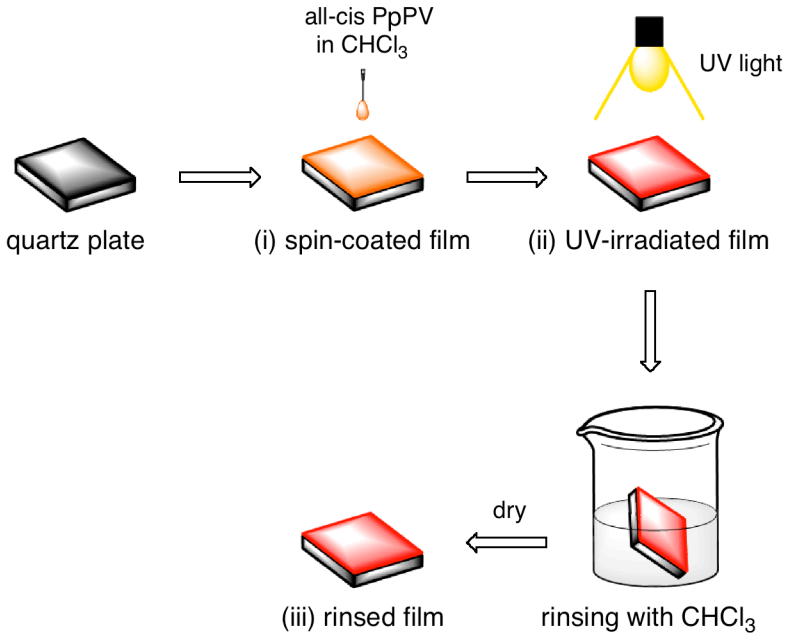


Figure 1. Experimental procedure for photo-induced insolubilization of all-cis PpPVs.

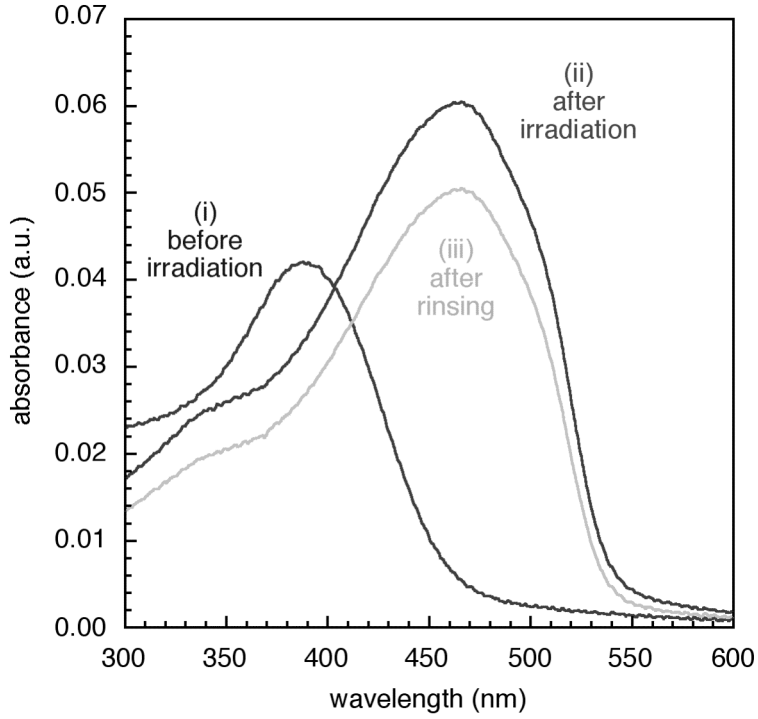


Figure 2. UV–vis absorption spectra of all-cis PpPV (**Ig**) in thin film, before and after UV-irradiation (i and ii), and after rinsing with $CHCl_3$ (iii).

to the percentage of PpPV insolubilized by UV-irradiation. The data for **Ia**–**h** and **IIa**–**c** are listed in Table 1.

Figure 3 plots the insolubilized PpPV percentages as the function of number-average molecular weights of the starting all-cis PpPVs. There are two lines of correlations, corresponding to type I and type II polymers, respectively. It is seen that type I polymers have much higher performance on insolubilization than type II polymers, showing a promotion effect of the (*Z*)-4-(2-bromoethenyl)phenyl group. It is also clear that the higher molecular weight polymer tends to remain in the higher percentage.

There is a possibility that the insolubilization is caused by cross-linking of polymer chains via photochemical reactions such as [2+2] cycloaddition of vinylene units and radical addition of C–Br bonds to vinylene linkages, where shortening of the effective π-conjugation length should occur to a considerable extent. However, no notable blue shifts of the λ_{max} values were observed for spectra (ii) and (iii) in Figure 2, as compared with that of all-trans PpPV (M_n = 7200, M_w/M_n = 1.81) independently prepared.[17]

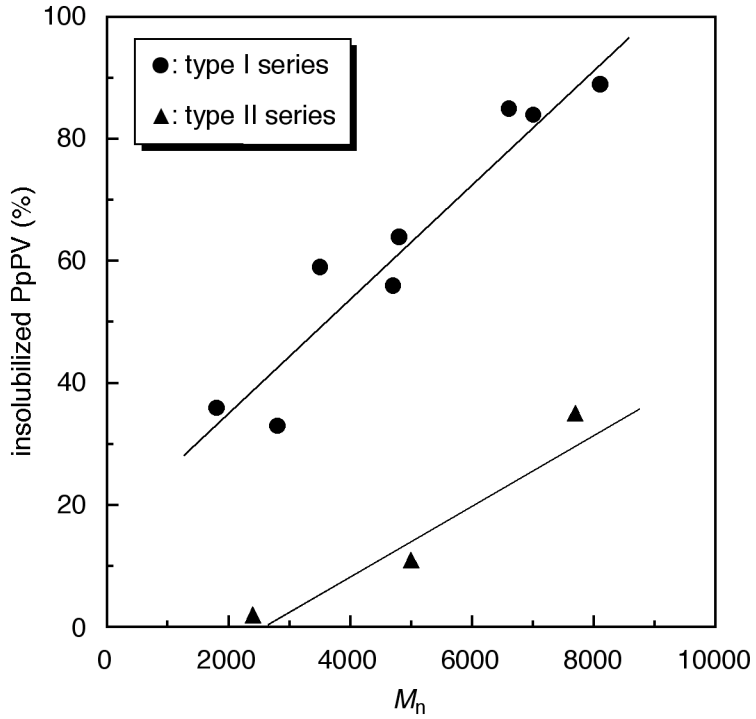


Figure 3. The relation between insolubilized PpPV percentages and number-average molecular weights of the starting all-cis PpPVs.

Therefore, the author considered an alternative mechanism of photo-induced insolubilization caused by supra-molecular interactions. It has been already confirmed that all-cis PpPV cast from a solution remains amorphous for a few hours.[16c] The amorphous all-cis PpPV has a low glass transition temperature (T_g; ca. 0 °C) and is in the liquid state at room temperature. Therefore, the all-cis PpPV molecules are expected to be highly mobile in thin films. In this situation, all-trans PpPV molecules generated by photo-isomerization will easily form a highly aligned structure with the aid of π–π stacking between the conjugated skeletons. It has been also known that halogen atoms on aromatic molecules facilitate the formation of π-stacks.[18] Thus the higher performance of type I polymer on insolubilization will be attributed to Br···Br interaction between PpPV molecules.

OFET Properties of Insolubilized PpPVs. The thin films of all-trans PpPVs formed by photo-induced insolubilization of all-cis PpPVs exhibited carrier mobility in OFET devices

Table 2. Carrier Mobility of PpPV Films before and after Photo-irradiation

entry	all-cis PpPV		carrier mobility (μ_{FET}, $cm^2\ V^{-1}\ s^{-1}$)		
	M_n [a]	M_w/M_n [a]	spin-coated film	UV-irradiated film	rinsed film
1	5900	3.61	$<10^{-6}$	1.0×10^{-6}	*c*
2	7700	2.69	$<10^{-6}$	2.3×10^{-5}	*c*
3	11200	2.66	$<10^{-6}$	5.0×10^{-5}	*c*
4	34600 [b]	1.47	$<10^{-6}$	5.0×10^{-5}	1.6×10^{-4}

[a] Determined by GPC calibration based on polystyrene standards. [b] Separated from an all-cis PpPV (M_n = 15700) by recycle GPC. [c] Not determined.

fabricated on Si–SiO_2 substrates (see Experimental Section).[19,20] Table 2 summarizes the results. Although all-cis PpPVs simply coated on substrates were insulators, they exhibited hole mobility after UV-irradiation at room temperature for 1 h. The mobility was improved with increasing molecular weights of the starting polymers, and further by rinsing the film with toluene (entry 4). It was also confirmed in a separate experiment that all-trans PpPV (M_n = 7200, M_w/M_n = 1.81) prepared by Hiyama-type polycondensation is an insulator even after photo-irradiation. These observations may also indicate the occurrence of molecular alignment during the photo-induced insolubilization of all-cis PPVs in thin films.

Conclusions

In conclusion, it has been confirmed that the performance on photo-induced insolubilization notably depends on molecular weights and terminal structures of the starting all-cis PPVs. Type I polymers with $M_n > 6600$ are insolubilized in 84–89% probability. The resulting films of all-trans PpPVs exhibited the carrier mobility of up to 1.6×10^{-4} $cm^2\ V^{-1}\ s^{-1}$ in OFET devices.

Experimental Section

General Considerations. All manipulations using organometallic compounds were carried out under a nitrogen or argon atmosphere using conventional Schlenk techniques. Nitrogen and argon gas were dried by passing through P_2O_5 (Merck, SICAPENT). Analytical GPC was carried out on a JASCO GPC assembly consisting of a model PU-980 precision pump, a model RI-1530 refractive index detector, and three polystyrene gel columns (Shodex KF-801, KF-803L, KF-805L). THF was used as the mobile phase with a flow rate of 1.0 mL/min at 40 °C. The columns were calibrated against 9 standard polystyrene samples (Shodex; M_n = 980–1,920,000). Recycling preparative GPC was carried out on a JAI LC918U equipped with two preparative GPC columns (JAIGEL-1H-A and -2H-A). $CHCl_3$ was used as the mobile phase with a flow rate of 3.8 mL/min. ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian Mercury 300 spectrometer, operating at 300.10 MHz. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University. Spin coating of PpPVs was performed with a Mikasa spin coater 1H-DX2. Photoirradiation was carried out at room temperature with an Asahi Spectra LAX-101 Xe lamp. UV-vis absorption spectra were recorded on a JASCO V-560 spectrometer.

Toluene was dried over sodium benzophenone ketyl, distilled, and stored over activated molecular sieves (MS4A). The following compounds were synthesized according to literatures: $Pd(PPh_3)_4$,[21] (*Z*,*Z*)-1,4-(2-bromoethenyl)benzene (**1**),[22] 2,5-dioctyloxybenzene-1,4-diboronic acid (**2**),[23] 2,5-dioctyloxybenzeneboronic acid (**5**),[24] and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dioctyloxybenzene.[16b] All-cis PpPVs (**Ia**–**h** and **IIa**)[16a,b] and all-trans PpPV[17] were prepared according to literatures. All other chemicals were obtained from commercial suppliers and used without further purification.

Photo-induced Insolubilization of PpPV. A solution of PpPV in $CHCl_3$ (2.0 wt%) was passed through a syringe filter (DISMIC-13 JP, PTFE 0.50 μm, Hydrophobic; ADVANTEC). A thin film of PpPV was prepared by spin coating on a quartz plate (1 cm^2); the filtrate (50 μL) was added dropwise on a plate, and the plate was accelerated to 1200 rpm

for 2 s, kept at this rate for 10 s, and then rotated at 2000 rpm for 60 s. After drying under vacuum at room temperature for 30 min, the film was placed in a quartz cell under N_2 atmosphere, and then analyzed by UV–vis absorption spectroscopy. Next, the film was placed in a stainless-steel holder with a quartz window, and irradiated by a Xe lamp (λ_{max} = 365 nm, 21.0 mW cm^{-2}) for 60 min under vacuum at room temperature. UV-vis absorption spectrum of the resulting film was then recorded. The film was rinsed twice in $CHCl_3$ (each 3 mL) with light shaking, dried under vacuum at room temperature, and examined by UV-vis absorption spectroscopy.

Preparation of all-cis PpPVs with High Molecular Weights (entries 3 and 4 in Table 2). (*Z*,*Z*)-**1** (173 mg, 0.600 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dioctyloxybenzene (352 mg, 0.600 mmol) and methyltrioctylammonium chloride (Aliquat® 336; 24.3 mg, 0.0600 mmol) were dissolved in toluene (3 mL), and 2.0 M aqueous Na_2CO_3 (0.90 mL, 1.8 mmol) and [Pd(PPh$_3$)$_4$] (10.4 mg, 9.00 μmol) were added. The mixture was vigorously stirred under reflux for 24 h in the dark. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (8 mL), washed with water, and then poured into a vigorously stirred MeOH/CH_2Cl_2 (5/1, 180 mL). A yellow precipitate of all-cis PpPV was collected by membrane filter (0.5 μm), washed with MeOH, and dried under vacuum at room temperature overnight (254 mg, 92% yield, M_n = 11200, M_w/M_n = 2.66). The polymer with M_n = 34600 (M_w/M_n = 1.47) was separated from this product by recycle GPC.

Measurement of Carrier Mobility. All manipulations were carried out in an argon-filled glove box. An OFET device was fabricated in a top-contact configuration on a *p*-type Si wafer as a gate electrode (one-side polished, < 0.02 Ω resistance, Furuuchi Chemical Co.) with 3000-Å-thick SiO_2 (C_i = 11 nF cm^{-2}) as a dielectric film. A plate was cut and washed in 2-propanol under ultrasonic wave and under boiling. A thin film of PpPVs as the active layer (ca. 30 nm thick) was deposited on the Si/SiO_2 substrate by spin-coating a 0.1–0.5 wt% solution in $CHCl_3$ at 100–8000 rpm for 60 s, and dried under vacuum at room temperature, and irradiated by a Xe lamp (λ_{max} = 365 nm, 23.0 mW cm^{-2}) for 1 h. On the top

of the thin film, gold films (30 nm) as source and drain electrodes were deposited through a mask. A drain-source channel length (L) and width (W) were 20 μm and 5 mm, respectively. Characteristics of OFET devices were evaluated at room temperature with two source meters (2400, Keithley Instruments Inc.). Carrier mobility (μ_{FET}) was calculated in the saturation regime (V_d = 100 V) of the I_d using the following equation,

$$I_d = (WC_i/2L)\ \mu_{FET}\ (V_g - V_t)^2$$

where C_i is the capacitance of the SiO_2 insulator, and V_g and V_t are the gate and threshold voltages, respectively. In another case, the PPV thin film was rinsed twice with toluene (1 mL) after UV-irradiation, and examined in a similar manner.

References and Notes

(1) (a) Richardson, T. H., Eds. *Functional Organic and Polymeric Materials*; John Wiley & Sons: Chichester, England, 2000. (b) Sheats, J. R.; Barbara, P. F., Eds. *Molecular Materials in Electronic and Optoelectronic Devices. Acc. Chem. Res.* **1999**, *32*, 191–276. (c) Müllen, K.; Scherf, U. Eds., *Organic Light Emitting Devices*; Wiley-VCH, Weinheim 2005. (d) Brüttig, W. Ed., *Physics of Organic Semiconductors*; Wiley-VCH, Weinheim 2005.

(2) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539–541. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402–428. (c) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897–1091.

(3) Veinot, J. G. C.; Marks, T. J. *Acc. Chem. Res.* **2005**, *38*, 632–643.

(4) Feng, K.; Tsushima, M.; Matsumoto, T.; Kurosaki, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 685–693.

(5) Bellmann, E.; Shaheen, S. E.; Thayumanavan, S.; Barlow, S.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. *Chem. Mater.* **1998**, *10*, 1668–1676.

(6) Chen, J. P.; Klaerner, G.; Lee, J.-I.; Markiewicz, D.; Lee, V. Y.; Miller, R. D.; Scott, J. C. *Synth. Met.* **1999**, *107*, 129–135.

(7) Li, W.; Wang, Q.; Cui, J.; Chou, H.; Shaheen, S. E.; Jabbour, G. E.; Anderson, J.; Lee, P.; Kippelen, B.; Peyghambarian, N.; Armstrong, N. R.; Marks, T. J. *Adv. Mater.* **1999**, *11*, 730–734.

(8) (a) Bayerl, M. S.; Braig, T.; Nuyken, O.; Müller, D. C.; Groß, M.; Meerholz, K. *Macromol. Rapid Commun.* **1999**, *20*, 224–228. (b) Müller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Ruudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. *Nature* **2003**, *421*, 829–833.

(9) Bacher, A.; Erdelen, C. H.; Paulus, W.; Ringsdorf, H.; Schmidt, H.-W.; Schuhmacher, P. *Macromolecules* **1999**, *32*, 4551–4557.

(10) Liu, S.; Jiang, X.; Ma, H.; Liu, M. S.; Jen, A. K.-Y. *Macromolecules* **2000**, *33*, 3514–3517.

(11) Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'iorio, M. *Chem. Mater.* **2003**, *15*, 4936–4943.

(12) Badarau, C.; Wang, Z. Y. *Macromolecules* **2004**, *37*, 147–153.

(13) Yang, C.; Hou, J.; Zhang, B.; Zhang, S.; He, C.; Fang, H.; Ding, Y.; Ye, J.; Li, Y. *Macromol. Chem. Phys.* **2005**, *206*, 1311–1318.

(14) Miyanishi, S.; Tajima, K.; Hashimoto, K. *Macromolecules* **2009**, *42*, 1610–1618.

(15) Roex, H.; Adriaensens, P.; Vanderzande, D.; Gelan, J. *Macromolecules* **2003**, *36,* 5613–5622.

(16) (a) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Umeda, K.; Akamatsu, K.; Tsuruoka, T.; Nawafune, H.; Ozawa, F. *J. Am. Chem. Soc.* **2005**, *127*, 4350–4353. (b) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Fukuse, Y.; Wakioka, M.; Ozawa, F. *Macromolecules* **2006**, *39*, 2039–2048. (c) Katayama, H.; Ozawa, F.; Matsumiya, Y.; Watanabe, H. *Polym. J.* **2006**, *38*, 184–189.

(17) Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet. Chem.* **2003**, *676*, 49–54.

(18) Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222–228.

(19) All-cis PpPVs with higher molecular weights (entries 3 and 4 in Table 2) were obtained by modified catalytic conditions reported in Experimental Section.

(20) For previous examples of OFETs using PpPVs, see: (a) Pichler, K.; Jarrett, C. P.; Friend, R. H.; Ratier, B.; Moliton, A. *J. Appl. Phys.* **1995**, *77*, 3523–3527. (b) Blom, P. W. M.; de Jong, M. J. M.; Vleggaar, J. J. M. *Appl. Phys. Lett.* **1996**, *68*, 3308–3310. (c) Geens, W.; Shaheen, S. E.; Wessling, B.; Brabec, C. J.; Poortmans, J.; Serdar Sariciftci, N. *Org. Electron.* **2002**, *3*, 105–110. (d) Roichman, Y.; Tessler, N. *Appl. Phys. Lett.* **2002**, *80*, 151–153. (e) Tzeng, K. L.; Meng, H. F.; Tzeng, M. F.; Chen, Y. S.; Liu, C. H.; Horng, S. F.; Yang, Y. Z.; Chang, S. M.; Hsu, C. S.; Chi, C. C. *Appl. Phys. Lett.* **2004**, *84*, 619–621. (f) Muratsubaki, M.; Furukawa, Y.; Noguchi, T.; Ohnishi, T.; Fujiwara, E.; Tada, H. *Chem. Lett.* **2004**, *33*, 1480–1481. (g) Chua, L.-L.; Zaumseil, J.; Chang, J.-F.; Ou, E. C.-W.; Ho, P. K.-H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194–199. (h) van Breemen, A. J. J. M.; Herwig, P. T.; Chlon, C. H. T.; Sweelssen, J.; Schoo, H. F. M.; Benito, E. M.; de Leeuw, D. M.; Tanase, C.; Wildeman, J.; Blom, P. W. M. *Adv. Funct. Mater.* **2005**, *15*, 872–876. (i) Tanase, C.; Wildeman, J.; Blom, P. W. M. *Adv. Funct. Mater.* **2005**, *15*, 2011–2015. (j) Tanase, C.; Wildeman, J.; Blom, P. W. M.; Mena, B. M. E.; de Leeuw, D. M.; van Breemen, A. J. J. M.; Herwig, P. T.; Chlon, C. H. T.; Sweelssen, J.; Schoo, H. F. M. *J. Appl. Phys.* **2005**, *97*, 123703/1–123703/6. (k) Todescato, F.; Capelli, R.; Dinelli, F.; Murgia, M.; Camaioni, N.; Yang, M.; Bozio, R.; Muccini, M. *J. Phys. Chem. B* **2008**, *112*, 10130–10136.

(21) Coulson, D. R. *Inorg. Synth.* **1971**, *13*, 121–124.

(22) Nagao, M.; Asano, K.; Umeda, K.; Katayama, H.; Ozawa, F. *J. Org. Chem.* **2005**, *70*, 10511–10514.

(23) Hu, Q.-S.; Huang, W.-S.; Vitharana, D.; Zheng, X.-F.; Pu, L. *J. Am. Chem. Soc.* **1997**, *119*, 12454–12464.

(24) Johansson, D. M.; Wang, X.; Johansson, T.; Inganaes, O.; Yu, G.; Srdanov, G.; Andersson, M. R. *Macromolecules* **2002**, *35*, 4997–5003.

Chapter 2

Stereocontrolled Synthesis and Photochemical Properties of All-cis and All-trans Poly(*m*-phenylenevinylene)s

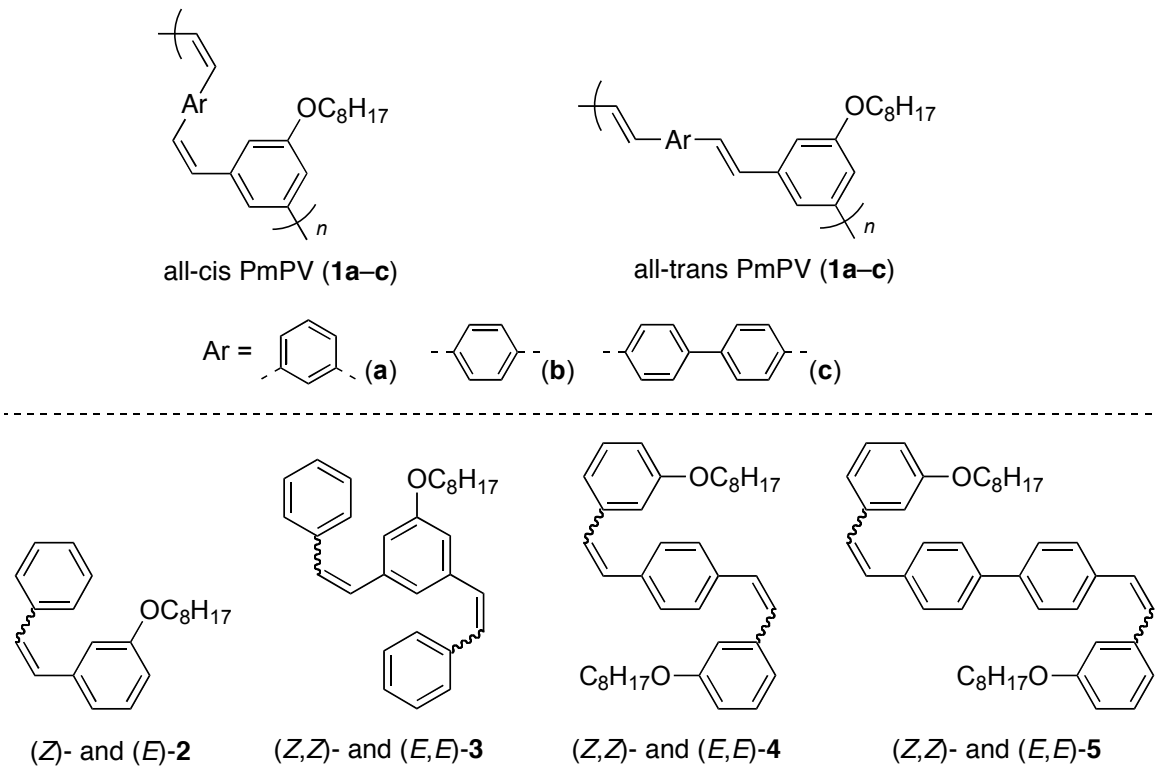
Abstract

All-cis and all-trans isomers of poly[(arylenevinylene)-*alt*-(5-octyloxy-1,3-phenylene-vinylene)]s having three kinds of arylene groups (PmPVs: arylene = *m*-phenylene (**1a**), *p*-phenylene (**1b**), 4,4'-biphenylene (**1c**)) have been synthesized in almost perfect stereoregularities by two types palladium-catalyzed polycondensation reactions. Suzuki–Miyaura-type polycondensation of (*Z*,*Z*)-bis(2-bromoethenyl)arenes with 5-octyloxy-1,3-benzenediboronic acid pinacolate affords all-cis **1a**–**c**, whereas Hiyama-type polycondensation of (*E*,*E*)-bis(2-silylethenyl)arenes with 5-octyloxy-1,3-diiodobenzene forms all-trans **1a**–**c**. The resulting polymers having relatively short effective π-conjugation lengths, interrupted by *m*-phenylene units, undergo two-way photoisomerization, giving PmPVs containing *cis*- and *trans*-vinylene groups in nearly 1:1 ratios, irrespective of the configurations of the staring polymers.

Introduction

The author's group recently succeeded for the first time in synthesizing all-cis poly(*p*-phenylenevinylene)s (PpPVs), in which vinylene linkages in the polymer chain are entirely stereoregulated to cis geometry.[1] The all-cis PpPVs are readily isomerized to the corresponding all-trans PpPVs in solution under UV-irradiation.[1a] The cis-to-trans isomerization also takes place when thin films of all-cis PpPVs are exposed to UV light. Interestingly, as described in Chapter 1, the PpPV films are insolubilized during the photoisomerization. Furthermore, the insolubilized films exhibit the carrier mobility (μ_{FET}) of up to 1.6×10^{-4} cm^2 V^{-1} s^{-1}. A key to this unique phenomenon is the "one-way photoisomerization" of PpPVs. The one-way photoisomerization of conjugated alkenes has been documented in several instances.[2,3] Thus, while stilbene undergoes two-way photo-isomerization to give a cis-rich mixture in the photostationary state, the alkenes with extended π-conjugation systems are isomerized solely from the cis to trans isomer.

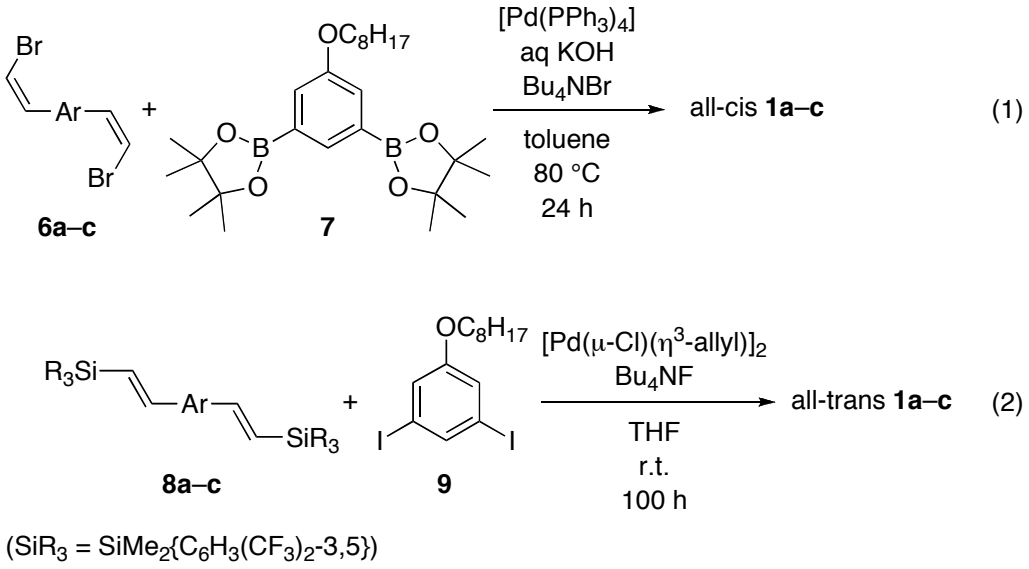
Chart 1



This chapter deals with the synthesis and photoisomerization of all-cis and all-trans poly(*m*-phenylenevinylene)s (PmPVs). Although photoisomerization of alkene has been extensively studied for small molecules, the related studies on polymeric alkenes have been scarce.[3] In this study, the author has compared photoisomerization behaviors between PmPVs (**1a**–**c**) and their constitution units (**2**–**5**) (Chart 1). Unlike PpPVs with extended π-conjugation systems, PmPVs have relatively short effective π-conjugation lengths, interrupted by *m*-phenylene units.[4] It has been found that PmPVs undergo two-way photoisomerization both in solution and in thin films.

Results and Discussion

Synthesis and Characterization of PmPVs. All-cis and all-trans PmPVs were synthesized by Suzuki–Miyaura-type[1,5] and Hiyama-type polycondensation,[6,7] respectively (eqs 1 and 2). The reactions of (*Z*,*Z*)-bis(2-bromoethenyl)arenes (**6a**–**c**) with 5-octyloxy-1,3-benzenediboronic acid ester (**7**) in toluene at 80 °C in the presence of [$Pd(PPh_3)_4$] (1.0 mol%), aqueous KOH (3 M, 3 equiv), and Bu_4NBr (1 equiv) for 24 h formed all-cis isomers of **1a**–**c** in 84–97% yields (entries 1–3 in Table 1). On the other hand, the reactions of (*E*,*E*)-bis(2-silylethenyl)arenes (**8a**–**c**) with 5-octyloxy-1,3-diiodobenzene (**9**) in THF at room temperature in the presence of [$Pd(\mu\text{-Cl})(\eta^3\text{-allyl})]_2$ (5 mol%) and Bu_4NF (2 equiv) for 100 h afforded all-trans isomers of **1a**–**c** in quantitative yields (entries 4–6 in Table 1).



The polymers were isolated as gummy pastes (all-cis PmPVs) or powdery solids (all-trans PmPVs), respectively. The geometry and stereoregularity of vinylene linkages were unequivocally confirmed by NMR spectroscopy. Table 2 compares the NMR data of **1a**–**c** with those of **2**–**5**. The vinylic carbons of cis and trans isomers showed clearly different chemical shifts at around δ 130 and 129, respectively. Moreover, the OCH_2 proton signals of octyloxy groups were well separated from each other. As seen from the ^1H NMR spectra in

Table 1. Synthesis of All-cis and All-trans PmPVs (**1a**–**c**)

entry	product	yield (%)[a]	M_n[b]	M_w/M_n[b]	cis/trans[c]
1	all-cis **1a**	97	3800	3.43	>99/1
2	all-cis **1b**	84	4300	4.23	>99/1
3	all-cis **1c**	95	4700	5.27	>99/1
4	all-trans **1a**	>99	5200	1.75	<1/99
5	all-trans **1b**	>99	4200	1.47	<1/99
6	all-trans **1c**	>99	8300	2.35	<1/99

[a] Isolated yield of MeOH-insoluble polymer. [b] Determined by GPC calibration based on polystyrene standards. [c] Determined by ^{1}H NMR.

Figure 1, the signals of *cis*- and *trans*-**1a** appeared at δ 3.59 and 4.03, respectively.[8,9] The cis/trans ratios listed in Table 1 were evaluated from the peak intensities of these signals.

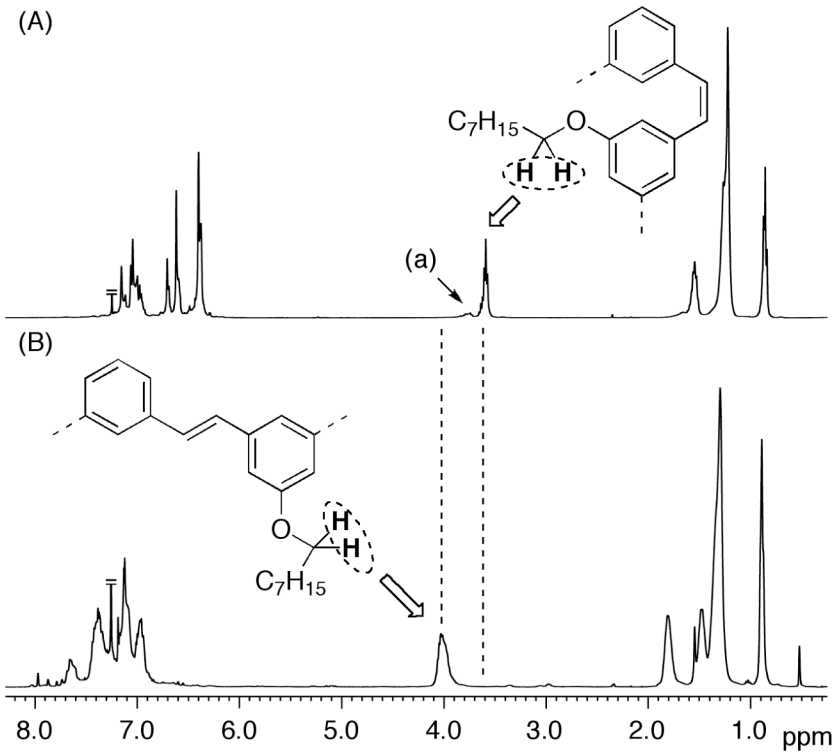


Figure 1. ^{1}H NMR spectra of (A) *cis*-**1a** and (B) *trans*-**1a** in $CDCl_3$ at room temperature.

Table 2. Selected NMR Data of PmPVs (**1a**–**c**) and Model Compounds (**2**–**5**)[a]

compound	^{13}C NMR $\delta_{C=C}$	^{1}H NMR δ_{OCH_2}
all-cis **1a**	130.1, 130.1	3.59
all-cis **1b**	130.0, 130.0	3.62
all-cis **1c**	130.4, 130.2	3.63
(*Z*)-**2**	130.3, 130.3	3.77
(*Z*,*Z*)-**3**	130.4, 130.0	3.59
(*Z*,*Z*)-**4**	130.2, 130.0	3.81
(*Z*,*Z*)-**5**	130.4, 129.8	3.80
all-trans **1a**	129.0, 128.8	4.03
all-trans **1b**	128.7, 128.5	4.05
all-trans **1c**	128.6, 128.6	4.07
(*E*)-**2**	128.9, 128.7	4.00
(*E*,*E*)-**3**	129.2, 128.5	4.05
(*E*,*E*)-**4**	128.6, 128.5	4.00
(*E*,*E*)-**5**	128.8, 128.4	4.01

[a] Measured in $CDCl_3$ at room temperature.

Photoisomerization of PmPVs. (a) In Solution. The all-cis and all-trans PmPVs were dissolved in benzene (4.0 mg L^{-1}) and irradiated with a Xe lamp (λ_{max} = 365 nm, 0.87 mW cm^{-2}) in a quartz cell under a nitrogen atmosphere at room temperature. The sample solutions were monitored at intervals by UV-vis spectroscopy. Figure 2 shows the change of absorption spectra of all-cis **1c** (A) and all-trans **1c** (B). Upon UV-irradiation, the absorption of all-cis isomer (λ_{max} = 328 nm) increased whereas that of all-trans isomer (λ_{max} = 366 nm) decreased to achieve the photostationary state.[10] The cis content in the equilibrium mixture was estimated as 53% according to the following equation: cis (%) = $(A_{trans} - A_{pss})/(A_{trans} - A_{cis}) \times 100$, where A_{trans} and A_{cis} stand for the absorbance of all-trans and all-cis isomers at

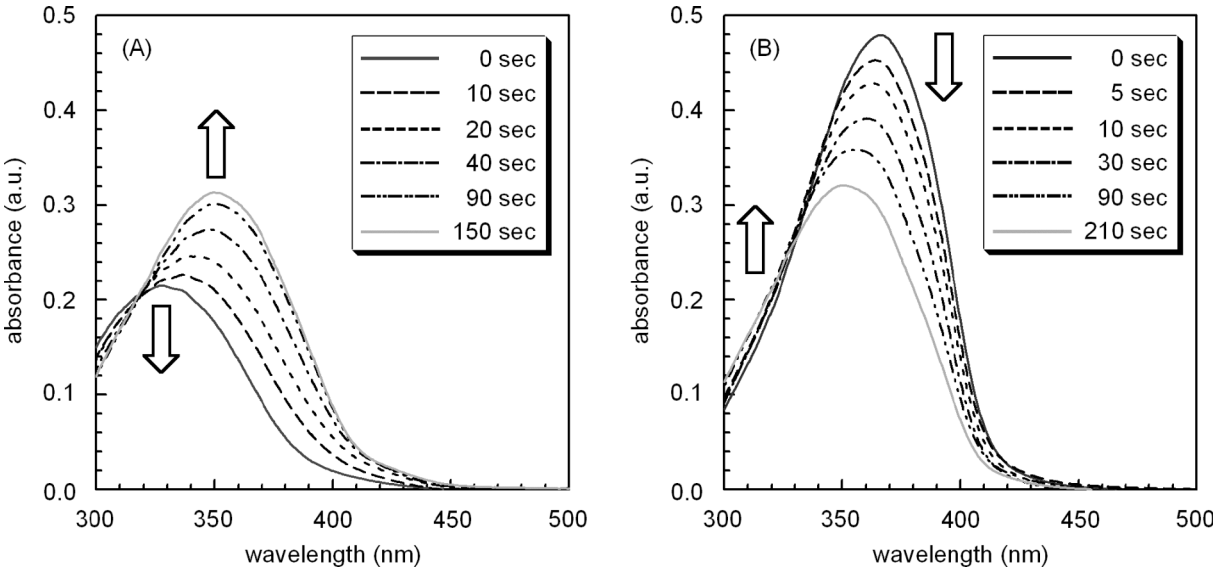


Figure 2. Changes of UV–vis absorption spectra of all-cis **1c** (A) and all-trans **1c** (B) under UV-irradiation in benzene (4.0 mg L^{-1}).

366 nm before UV-irradiation, respectively, and A_{pss} for the absorbance at the same wavelength in the photostationary state.

Table 3 summarizes the results of photoisomerization of **1a**–**c**. All polymers undergo two-way photoisomerization to give PmPVs containing *cis*- and *trans*-vinylene groups. It is seen that the cis/trans ratios in the photostationary state ($[cis/trans]_{pss}$) are quite different from those of **2**–**5**. Meeting the general expectations,[2] the trans contents in **2**–**5** in the photostationary state increase with elongation of the effective π-conjugation lengths in the order **2** < **3** < **4** < **5**. In contrast, the cis/trans ratios of **1a**–**c** converge at nearly 1:1 irrespective of the arylene groups. Since the λ_{max} values of **1a**–**c** are in good agreement with those of **3**–**5**, respectively, it is convincing that each polymer has almost the same π-conjugation length as the corresponding constitution. Nevertheless, the vinylene groups reach the equilibrium in a nearly 1:1 ratio.

It is known that the two-way photoisomerization of stilbene proceeds mainly via a singlet excited state with the 90°-twisted form as the potential minimum. The deactivation takes places solely from this perpendicular conformation to give a mixture of cis and trans isomers.[2] However, when the alkene unit is integrated into an extended π-conjugated system,

Table 3. Photoisomerization of **1a–c** and **2–5** in Benzene[a]

compound	λ_{max} (nm)			time (sec)[c]	cis/trans[d]
	all-cis	all-trans	pss[b]		
1a	273[e]	311	307	90	54/46
1b	319	372	368	330	46/54
1c	328	366	350	150	53/47
2	280[e]	310	——[f]	30	86/14
3	269[e]	313	——[f]	30	31/69
4	318	362	362	150	4/96
5	328	356	356	150	< 1/99

[a] A benzene solution of the compound (4.0 mg L^{-1}) was irradiated with a Xe lamp (λ_{max} = 365 nm, 0.87 mW cm^{-2}) in a quartz cell under a nitrogen atmosphere at room temperature. Photoisomerization was followed by UV-vis spectroscopy. [b] pss = photostationary state. [c] The time to achieve the photostationary state starting from cis isomer. [d] See text. [e] Measured in CH_2Cl_2. [f] Unable to be observed due to overlap with the absorbance of benzene.

the alkene molecule possibly undergoes intersystem crossing to give a triplet excited state, where the 90°-twisted form is no longer the potential minimum, and therefore the alkene molecule changes its conformation from the cis form to the trans form, passing through the perpendicular triplet state. As a result, the one-way photoisomerization becomes predominant to give a trans-rich or all-trans product. The variation in the cis/trans ratios observed for **2–5** is fully consistent with this trend. On the other hand, as for the polymeric alkenes **1a–c**, there is a possibility that the 90°-twisted form still remains as the energy minimum on the excited potential surface to avoid the steric congestion within the molecule. In this case, the excited state should be deactivated from the twisted form to give PmPVs containing both *cis*- and *trans*-vinylene groups.

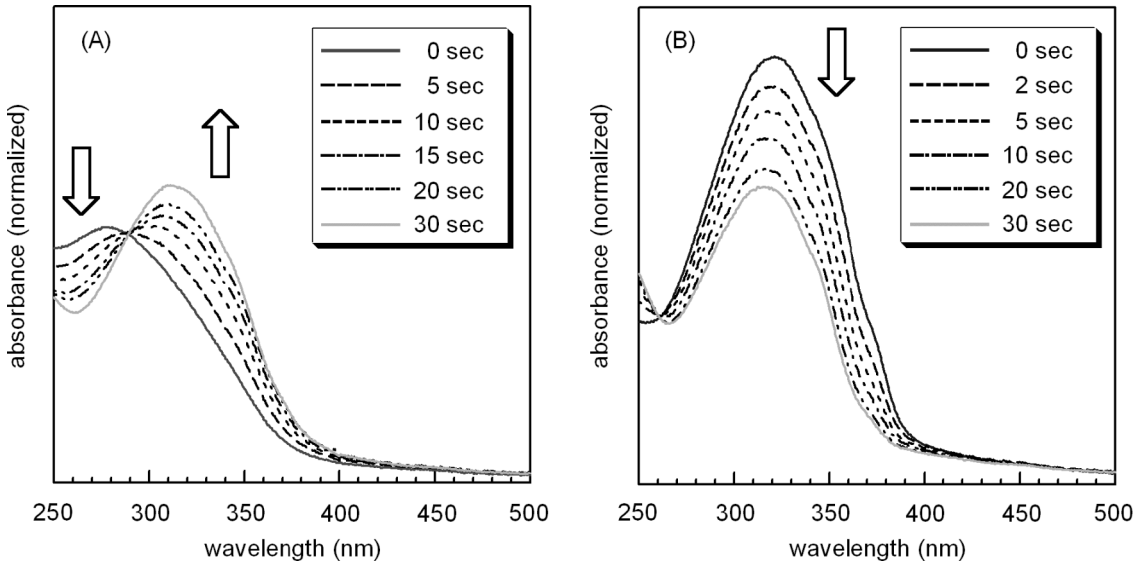


Figure 3. Changes of UV–vis absorption spectra of all-cis **1a** (A) and all-trans **1a** (B) under UV-irradiation in thin films.

(b) In Thin Films. All-cis and all-trans PmPVs underwent two-way photoisomerization in thin films as well. Figure 3 shows the change of UV-vis absorption spectra of **1a** in thin films, which were prepared from a $CHCl_3$ solution (2.0 wt%) by spin-coating on a quartz substrate, and irradiated with a Xe lamp (λ_{max} = 365 nm, 21.0 mW cm^{-2}) under vacuum at room temperature. It was noted that the absorption maxima of all-cis and all-trans **1a** are red-shifted by 2 and 11 nm, respectively, as compared with those in solution. Although the photoisomerization could not be evaluated quantitatively because of the change of the thickness of films depending on the experimental runs, the spectroscopic change in this figure indicates a very similar cis/trans ratio to the solution system. Interestingly, the photo-irradiated films remained on the substrate in high percentages (>90%) after rising twice with $CHCl_3$. Thus, PmPVs were found to undergo photo-induced insolubilization in thin films.

Conclusions

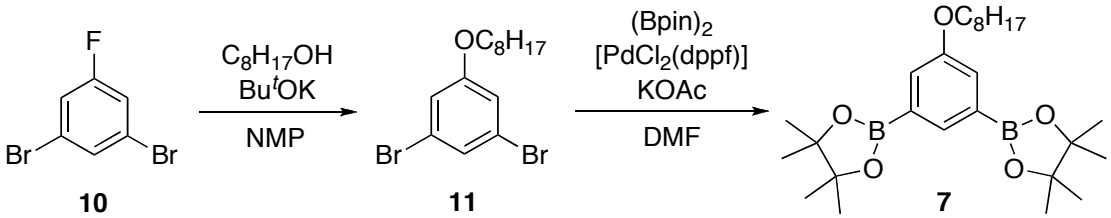
Suzuki–Miyaura-type and Hiyama-type polycondensation reactions provide all-cis and all-trans PmPVs in perfect stereoregularity, respectively. The resulting polymers undergo two-way photoisomerization of vinylene units in solution as well as in thin films, giving PmPVs containing *cis*- and *trans*-vinylene groups in nearly 1:1 ratios. This behavior is quite different from that of the corresponding poly(*p*-phenylenevinylene)s (PpPVs), which undergo one-way photoisomerization to all-trans isomers in the photostationary state. Thus, it has been evidenced that the photoisomerization behaviors of poly(phenylenevinylene)s are dependent on the effective π-conjugation lengths of polymer chains.

Experimental Section

General Considerations. All manipulations using organometallic compounds were carried out under a nitrogen or argon atmosphere using conventional 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 and ^{13}C NMR 100.62 MHz). Chemical shifts are reported in δ (ppm), referenced to the ^{1}H (residual protons) and ^{13}C signals of deuterated solvents. Mass spectra were measured with a Shimadzu QP-500 GC-mass spectrometer (EI, 70 eV) or Shimadzu GC-MS QP2010 (EI, 70 eV). Melting points were measured with a Yanaco MP-S3 instrument. Analytical GPC was carried out on a JASCO GPC assembly consisting of a model PU-980 precision pump, a model RI-1530 refractive index detector, and three polystyrene gel columns (Shodex KF-801, KF-803L, KF-805L). THF was used as the mobile phase with a flow rate of 1.0 mL min^{-1} at 40 °C. The columns were calibrated against 9 standard polystyrene samples (Shodex; M_n = 980–1920000). Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University. Spin-coating of PmPV was performed with a Mikasa spin coater 1H-DX2. Photo-irradiation was carried out at room temperature with an Asahi Spectra LAX-101 Xe lamp. UV-vis absorption spectra were recorded on a JASCO V-560 spectrometer.

Toluene was dried over sodium benzophenone ketyl, distilled, and stored over activated molecular sieves (MS4A). THF (Wako, dehydrated) was used as received. The following compounds were synthesized according to literatures: $[Pd(PPh_3)_4]$,[11] $[Pd(\mu\text{-Cl})(\eta^3\text{-allyl})]_2$,[12] $[RuHCl(CO)(PPh_3)_3]$,[13] (*Z*,*Z*)-bis(2-bromoethenyl)arenes (**6a**–**c**),[14] (*E*,*E*)-1,4-bis[2-{(3,5-bis-(trifluoromethyl)phenyl)dimethylsilyl}ethenyl]benzene (**8b**),[7] dimethyl[3,5-bis(trifluoro-methyl)phenyl]silane,[15] 4,4'-diethynylbiphenyl (**12**),[16] (*Z*)-styryl bromide (**17**),[17] and (*E*)-[2-{(3,5-bis(trifluoromethyl)phenyl)dimethylsilyl}ethenyl]benzene (**20**)[18] All other chemicals were obtained from commercial suppliers and used without further purification.

Synthesis of Monomers. (a) 1,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -5-octyloxybenzene (7).[19]

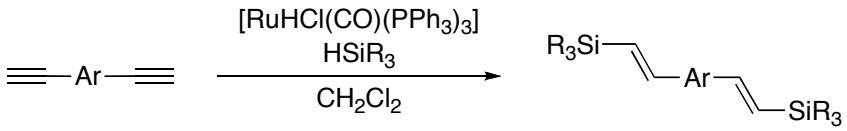


This compound was prepared by a two-step procedure. (i) To a solution of 1,3-dibromo-5-fluorobenzene (**10**; 9.02 g, 35.5 mmol) and *N*-methylpyrrolidione (4.93 g, 49.8 mmol) in 1-octanol (35.5 mL) was added potassium *tert*-butoxide (14.0 g, 124 mmol) at 0 °C. The mixture was stirred at 0 °C for 15 min, and then at room temperature for 4 h. Water (50 mL) was added, and the resulting mixture was extracted with Et_2O (4 × 75 mL). The combined extracts were washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Remaining 1-octanol was removed by bulb-to-bulb distillation (35 Pa, 55 °C). The residue was purified by flash column chromatography (SiO_2, hexane) to afford 1,3-dibromo-5-octyloxybenzene (**11**) as a colorless oil (11.9 g, 92% yield). ^1H NMR ($CDCl_3$): δ 7.22 (t, *J* = 1.6 Hz, 1H, H^2 of Ar), 6.98 (d, *J* = 1.7 Hz, 2H, $H^{3,5}$ of Ar), 3.91 (t, *J* = 6.5 Hz, 2H, OCH_2), 1.76 (m, 2H, CH_2), 1.45–1.29 (several m, 10H, CH_2), 0.91–0.87 (m, 3H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 160.3 (s, C^5 of Ar), 126.1 (s, $C^{1,3}$ of Ar), 123.0 (s, C^2 of Ar), 116.9 (s, $C^{4,6}$ of Ar), 68.6 (s, OCH_2), 31.8, 29.2, 29.2, 29.0, 25.9, 22.6

(each s, CH_2), 14.1 (s, CH_3). MS, *m*/*z* (relative intensity, %): 364 (M^+, 6), 254 (14), 252 (30), 250 (16), 83 (15), 71 (22), 70 (21), 69 (14), 57 (50), 56 (20), 55 (37), 43 (90), 42 (17), 41 (100). Anal. Calcd. for $C_{14}H_{20}Br_2O$: C, 40.90; H, 4.90. Found: C, 40.78; H, 4.78.

(ii) A mixture of **11** (3.96 g, 10.9 mmol), bis(pinacolato)diboron (6.07 g, 23.9 mmol), [$PdCl_2$(dppf)] (477 mg, 0.652 mmol), potassium acetate (6.40 g, 65.2 mmol), and DMF (109 mL) was stirred at 80 °C for 5 h. The solvent was removed by bulb-to-bulb distillation (5 kPa, 70 °C). The residue was dissolved in CH_2Cl_2, filtered though a Celite pad, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (SiO_2) eluted with CH_2Cl_2/hexane (9/1, 1% Et_3N), and subsequently recrystallized from CH_2Cl_2/pentane at –30 °C to afford **7** as a white solid (2.42 g, 48% yield). Mp: 55 °C. ^{1}H NMR ($CDCl_3$): δ 7.85 (s, 1H, H^2 of Ar), 7.42 (s, 2H, $H^{4,6}$ of Ar), 3.99 (t, *J* = 6.4 Hz, 2H, OCH_2), 1.80–1.71 (m, 2H, CH_2), 1.50–1.25 (several m, 10H, CH_2), 1.33 (s, 24H, $C(CH_3)_2$), 0.91–0.87 (m, 3H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 158.2 (s, C^5 of Ar), 133.4 (s, C^2 of Ar), 123.4 (s, $C^{4,6}$ of Ar), 83.7 (s, $C(CH_3)_2$), 67.8 (s, OCH_2), 31.8, 29.4, 29.3, 29.3, 26.1 (each s, CH_2), 24.8 (s, $C(CH_3)_2$), 22.7 (s, CH_2), 14.1 (s, CH_3). MS, *m*/*z* (relative intensity, %): 459 (M^+ + 1, 5), 458 (M^+, 17), 457 (M^+ – 1, 8), 260 (14), 101 (10), 83 (41), 69 (16), 59 (14), 57 (40), 55 (42), 43 (100), 42 (24), 41 (72). Anal. Calcd. for $C_{26}H_{44}B_2O_5$: C, 68.15; H, 9.68. Found: C, 67.90; H, 9.88.

(b) (*E*,*E*)-Bis[2-{(3,5-bis(trifluoromethyl)phenyl)dimethylsilyl}ethenyl]arenes (8).[7]



12a,**c** (SiR$_3$ = SiMe$_2${C$_6$H$_3$(CF$_3$)$_2$-3,5}) **8a**,**c**

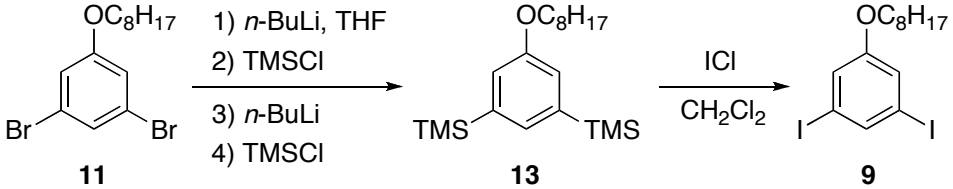
A typical procedure is reported for **8a**. To a solution of dimethyl-[3,5-bis(trifluoromethyl)phenyl]silane (3.01 g, 11.0 mmol) and 1,3-diethynylbenzene (**12a**; 253 mg, 2.01 mmol) in CH_2Cl_2 (8 mL) was added [$RuHCl(CO)(PPh_3)_3$] (191 mg, 0.201 mmol). The mixture was stirred for 5 h, and concentrated under reduced pressure. The

residue was subjected to flash column chromatography (SiO_2) eluted with hexane/CH_2Cl_2 (40/1). The crude product was purified by recycle GPC to afford **8a** as a colorless oil (745 mg, 53% yield, (*E*,*E*) > 99%). Compound **8c** was similarly prepared and isolated as a pale yellow solid by recrystallization from CH_2Cl_2/hexane (85% yield).

8a. ^{1}H NMR ($CDCl_3$): δ 7.97 (br s, 4H, $H^{2,6}$ of C_6H_3), 7.87 (br s, 2H, H^4 of C_6H_3), 7.57 (s, 1H, H^2 of C_6H_4), 7.42–7.39 (m, 2H, $H^{4,6}$ of C_6H_4), 7.34 (dd, J = 8.6, 6.4 Hz, 1H, H^5 of C_6H_4), 7.00 (d, J = 19.2 Hz, 2H, C_6H_4CH=), 6.57 (d, J = 19.1 Hz, 2H, =CHSi), 0.52 (s, 12H, $Si(CH_3)_2$). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 146.5 (s, C_6H_4CH=), 142.3 (s, C^1 of C_6H_3), 138.0 (s, $C^{1,3}$ of C_6H_4), 133.6 (s, $C^{2,6}$ of C_6H_3), 130.9 (q, $^2J_{FC}$ = 33 Hz, $C^{3,5}$ of C_6H_3), 129.0 (s, C^5 of C_6H_4), 126.9 ($C^{4,6}$ of C_6H_4), 125.2 (s, =CHSi), 124.9 (s, C^2 of C_6H_4), 123.6 (q, $^1J_{FC}$ = 273 Hz, CF_3), 122.9 (septet, $^3J_{FC}$ = 4 Hz, C^4 of C_6H_3), –2.8 (s, $Si(CH_3)_2$). Anal. Calcd. for $C_{30}H_{26}F_{12}Si_2$: C, 53.72; H, 3.91. Found: C, 53.52; H, 3.86.

8c. Mp: 144 °C. ^{1}H NMR ($CDCl_3$): δ 7.97 (br s, 4H, $H^{2,6}$ of C_6H_3-3,5-$(CF_3)_2$), 7.87 (br s, 2H, H^4 of C_6H_3-3,5-$(CF_3)_2$), 7.61 (d, J = 8.3 Hz, 4H, $H^{2,6,2',6'}$ of $C_{12}H_8$), 7.54 (d, J = 8.4 Hz, 4H, $H^{3,5,3',5'}$ of $C_{12}H_8$), 7.02 (d, J = 19.1 Hz, 2H, C_6H_4CH=), 6.57 (d, J = 19.1 Hz, 2H, =CHSi), 0.52 (s, 12H, $Si(CH_3)_2$). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 146.3 (s, C_6H_4CH=), 142.4 (s, C^1 of C_6H_3-3,5-$(CF_3)_2$), 140.7 (s, $C^{1,1'}$ of $C_{12}H_8$), 136.8 (s, $C^{4,4'}$ of $C_{12}H_8$), 133.6 (s, $C^{2,6}$ of C_6H_3-3,5-$(CF_3)_2$), 130.8 (q, $^2J_{FC}$ = 33 Hz, $C^{3,5}$ of C_6H_3-3,5-$(CF_3)_2$), 127.7, 127.2 (each s, $C^{2,6,2',6'}$ and $C^{3,5,3',5'}$ of $C_{12}H_8$), 124.8 (s, =CHSi), 123.9 (q, $^1J_{FC}$ = 273 Hz, CF_3), 122.9 (septet, $^3J_{FC}$ = 4 Hz, C^4 of C_6H_3-3,5-$(CF_3)_2$), –2.8 (s, $Si(CH_3)_2$). Anal. Calcd. for $C_{36}H_{30}F_{12}Si_2$: C, 57.90; H, 4.05. Found: C, 57.75; H, 4.25.

(c) 1,3-Diiodo-5-octyloxybenzene (9).



This compound was prepared by a two-step procedure. (i) To a solution of **11** (7.91 g, 21.7 mmol) in THF (109 mL) was added dropwise a 1.59 M solution of *n*-BuLi in hexane (14.2 mL, 22.4 mmol) at –78 °C. After the mixture was stirred at this temperature for 1 h, trimethylsilyl chloride (3.1 mL, 24 mmol) was slowly added. The solution was stirred at –78 °C for 1 h and then at room temperature for 1 h. This process was repeated with a 1.59 M solution of *n*-BuLi in hexane (16.5 mL, 26.0 mmol) and trimethylsilyl chloride (3.1 mL, 24 mmol). Water (200 mL) was added, and the mixture was extracted with diethyl ether (4 × 100 mL). The combined extracts were washed with brine (100 mL), dried over $MgSO_4$, evaporated under reduced pressure, and then purified by flash column chromatography (SiO_2, hexane) to give 1,3-bis(trimethylsilyl)-5-octyloxybenzene (**13**) as a colorless oil (7.32 g, 96% yield). ^{1}H NMR ($CDCl_3$): δ 7.22 (t, J = 0.9 Hz, 1H, H^4 of Ar), 7.03 (d, J = 0.8 Hz, 2H, $H^{2,6}$ of Ar), 3.98 (t, J = 6.6 Hz, 2H, OCH_2), 1.83–1.74 (m, 2H, CH_2), 1.52–1.24 (several m, 10H, CH_2), 0.92–0.86 (m, 3H, CH_3), 0.27 (s, 18H, $Si(CH_3)_3$). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 157.9 (s, C^1 of Ar), 141.3 (s, C^4 of Ar), 130.2 (s, $C^{3,5}$ of Ar), 119.6 (s, $C^{2,6}$ of Ar), 67.7 (s, OCH_2), 31.8, 29.4, 29.4, 29.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3), –1.1 (s, $Si(CH_3)_3$). MS, *m*/*z* (relative intensity, %): 352 (M^+ + 2, 4), 351 (M^+ + 1, 10), 350 (M^+, 29), 336 (11), 335 (35), 238 (13), 225 (6), 224 (16), 223 (70), 179 (10), 75 (9), 74 (9), 73 (100), 69 (28), 57 (21), 55 (35), 45 (26), 43 (86), 41 (78). Anal. Calcd. for $C_{20}H_{38}OSi_2$: C, 68.50; H, 10.92. Found: C, 68.73; H, 10.74.

(ii) To a solution of **13** (6.42 g, 18.3 mmol) in CH_2Cl_2 (92 mL) was added dropwise a 1.0 M solution of iodine chloride in CH_2Cl_2 (55 mL, 55 mmol) at –78 °C. The reaction solution was stirred at this temperature for 2 h. An aqueous $Na_2S_2O_3$ solution (10%, 100 mL) was added, and the mixture was extracted with CH_2Cl_2 (4 × 100 mL). The combined extracts were washed with brine (100 mL), dried over $MgSO_4$, and evaporated under reduced pressure, to give a pale yellow solid, which was purified by flash column chromatography (SiO_2, hexane), and subsequently recrystallized from $CHCl_3$/EtOH at –30 °C to afford **9** as a white solid (6.69 g, 80% yield). Mp: 37 °C. ^{1}H NMR ($CDCl_3$): δ 7.60 (t, J = 1.2 Hz, 1H, H^2 of Ar), 7.20 (d, J = 1.2 Hz, 2H, $H^{4,6}$ of Ar), 3.88 (t, J = 6.5 Hz, 2H, OCH_2), 1.79–1.70 (m, 2H, CH_2),

1.46–1.24 (several m, 10H, CH_2), 0.92–0.86 (m, 3H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 159.9 (s, C^5 of Ar), 137.2 (s, C^2 of Ar), 123.4 (s, $C^{4,6}$ of Ar), 94.6 (s, $C^{1,2}$ of Ar), 68.5 (s, OCH_2), 31.8, 29.3, 29.2, 29.0, 25.9, 22.6 (each s, CH_2), 14.1 (s, CH_3). MS, *m*/*z* (relative intensity, %): 459 (M^+ + 1, 2), 458 (M^+, 13), 347 (3), 346 (45), 75 (13), 69 (12), 63 (19), 57 (33), 55 (31), 43 (82), 42 (11), 41 (100). Anal. Calcd. for $C_{14}H_{20}I_2O$: C, 36.70; H, 4.40. Found: C, 36.59; H, 4.46.

Synthesis of All-cis PmPVs (1). A typical procedure is reported for all-cis **1a**. To a solution of **6a** (28.8 mg, 0.100 mmol), **7** (45.8 mg, 0.100 mmol), and Bu_4NBr (32.2 mg, 0.100 mmol) in toluene (0.5 mL) were added [$Pd(PPh_3)_4$] (1.2 mg, 1.0 μmol) and 3.0 M aqueous KOH (0.10 mL, 0.30 mmol). The mixture was stirred at 80 °C for 24 h in the dark. The mixture was extracted with CH_2Cl_2 (1 mL), washed with water (3 × 3 mL), and then poured into a vigorously stirred MeOH (50 mL). A pale yellow, sticky precipitate of all-cis **1a** was collected by decantation, washed with MeOH, and dried under vacuum at room temperature overnight (32.3 mg, 97% yield).

All-cis 1a. Pale yellow gummy paste. ^1H NMR ($CDCl_3$): δ 7.20–6.90 (m, C_6H_4), 6.73–6.67 (m, H^2 of C_6H_3OR), 6.64–6.57 (m, $H^{4,6}$ of C_6H_3OR), 6.44–6.32 (m, CH=CH), 3.84–3.70 (m, OCH_2 of terminal C_6H_4OR), 3.59 (t, *J* = 6.5 Hz, OCH_2), 1.80–1.49 and 1.43–1.14 (m, CH_2), 0.92–0.80 (m, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.7 (s, C^5 of C_6H_3OR), 138.3 (s, $C^{1,3}$ of C_6H_3OR), 137.1 (s, $C^{1,3}$ of C_6H_4), 130.1, 130.1 (each s, CH=CH), 129.7 (s, C^5 of C_6H_4), 127.8 (s, C^2 of C_6H_4), 127.6 (s, $C^{4,6}$ of C_6H_4), 122.2 (s, C^2 of C_6H_3OR), 113.8 (s, $C^{4,6}$ of C_6H_3OR), 67.8 (s, OCH_2), 31.9, 29.3, 29.3, 29.1, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3).

All-cis 1b. Yellow gummy paste. ^1H NMR ($CDCl_3$): δ 7.06 (br, C_6H_4), 6.74 (br, H^2 of C_6H_3OR), 6.62 (br, $H^{4,6}$ of C_6H_3OR), 6,43 (br, CH=CH), 3.62 (t, *J* = 6.3 Hz, OCH_2), 1.73–1.53 and 1.43–1.16 (m, CH_2), 0.92–0.80 (m, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.8 (s, C^5 of C_6H_3OR), 138.5 (s, $C^{1,3}$ of C_6H_3OR), 135.9 (s, $C^{1,4}$ of C_6H_4), 130.0, 130.0 (each s, CH=CH), 128.9 (s, $C^{2,3,5,6}$ of C_6H_4), 121.8 (s, C^2 of C_6H_3OR), 113.7 (s, $C^{4,6}$ of C_6H_3OR), 83.8

(s, *C*(CH_3)$_2$ of terminal BOC(CH_3)$_2$), 67.8 (s, OCH_2), 31.8, 29.3, 29.3, 29.1, 25.9 (each s, CH_2), 24.8 (s, C(*C*H_3)$_2$ of terminal BOC(CH_3)$_2$), 22.7, 14.1 (s, CH_3).

All-cis 1c. Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.52–7.15 (m, $H^{2,6,2',6'}$ and $H^{3,5,3',5'}$ of $C_{12}H_8$), 6.83 (br, H^6 of C_6H_3OR), 6.68 (br, $H^{2,4}$ of C_6H_3OR), 6.53–6.42 (m, CH=CH), 3.63 (br, 2H, OCH_2), 1.74–1.47 (br, 2H, CH_2), 1.45–1.07 (br, 10H, CH_2), 1.31 (s, C(CH_3)$_2$ of terminal BOC(CH_3)$_2$), 0.92–0.74 (br, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.9 (s, C^3 of C_6H_3), 139.1, 138.6, 136.1 (each s, $C^{1,1'}$ and $C^{4,4'}$ of $C_{12}H_8$ and $C^{1,5}$ of C_6H_3), 130.4, 130.2 (each s, CH=CH), 129.4, 126.4 (each s, $C^{2,6,2',6'}$ and $C^{3,5,3',5'}$ of C_8H_{12}), 121.7 (s, C^6 of C_6H_3), 113.8 (s, $C^{2,4}$ of C_6H_3), 83.8 (s, *C*(CH_3)$_2$ of terminal BOC(CH_3)$_2$), 67.8 (s, OCH_2), 31.8, 29.3, 29.2, 29.1, 25.9, 22.7 (each s, CH_2), 24.8 (s, C(*C*H_3)$_2$ of terminal BOC(CH_3)$_2$), 14.1 (s, CH_3).

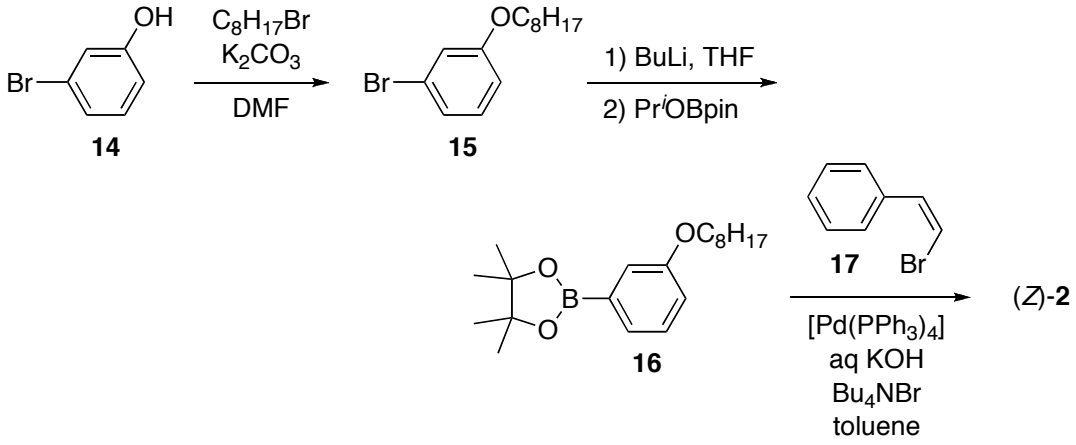
Synthesis of All-trans PmPVs (1). A typical procedure is reported for of all-trans **1a**. To a solution of **8a** (67.7 mg, 0.100 mmol) and **9** (45.4 mg, 0.100 mmol) in THF (1.0 mL) were added [Pd(μ-Cl)(η^3-allyl)]$_2$ (1.8 mg, 5.0 μmol) and a 1.0 M solution of $Bu_4NF{\cdot}3H_2O$ in THF (0.20 mL, 0.20 mmol). The mixture was stirred at room temperature for 100 h. The resulting suspension was poured into a vigorously stirred MeOH (50 mL). A white precipitate of all-trans **1a** was collected by a membrane filter (0.5 μm), washed with MeOH, and dried under vacuum at room temperature overnight (36.0 mg, >99% yield).

All-trans 1a. White solid. ^{1}H NMR ($CDCl_3$): δ 8.03 (br s, $H^{2,6}$ of C_6H_3-3,5-(CF_3)$_2$ of terminal CH=CHSi(CH_3)$_2$Ar), 7.87 (br s, H^4 of C_6H_3-3,5-(CF_3)$_2$ of terminal CH=CHSi(CH_3)$_2$Ar), 7.71–7.57 (m, H^3 of C_6H_4), 7.50–7.25 (m, $H^{4,6}$ and H^5 of C_6H_4), 7.25–7.04 (m, H^2 of C_6H_3OR and CH=CH), 7.04–6.86 (m, $H^{2,6}$ of C_6H_3OR), 4.11–3.88 (m, OCH_2), 1.90–1.73 and 1.57–1.20 (m, CH_2), 0.93–0.83 (m, CH_3), 0.52 (s, CH_3 of terminal CH=CHSi(CH_3)$_2$Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.8 (s, C^5 of C_6H_3OR), 138.8 (s, $C^{1,3}$ of C_6H_3OR), 137.6 (s, $C^{1,3}$ of C_6H_4), 129.0, 128.8 (each s, CH=CH), 128.8 (s, C^2 of C_6H_4), 125.9 (s, $C^{4,6}$ of C_6H_4), 124.8 (s, C^5 of C_6H_4), 118.0 (s, C^2 of C_6H_3OR), 111.8 (s, $C^{4,6}$ of C_6H_3OR), 68.1 (s, OCH_2), 31.9, 29.4, 29.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3), –2.8 (s, CH_3 of terminal CH=CHSi(CH_3)$_2$Ar).

All-trans 1b. Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.97 (br s, $H^{2,6}$ of C_6H_3-3,5-$(CF_3)_2$ of terminal CH=CHSi$(CH_3)_2$Ar), 7.87 (br s, H^4 of C_6H_3-3,5-$(CF_3)_2$ of terminal CH=CHSi$(CH_3)_2$Ar), 7.54 (s, C_6H_4), 7.20–7.03 (m, H^2 of C_6H_3 and CH=CH), 6.99 (s, $H^{2,6}$ of C_6H_3), 4.05 (t, J = 6.4 Hz, OCH_2), 3.95 (t, J = 6.4 Hz, OCH_2 of terminal $C_6H_3IOC_8H_{17}$), 1.90–1.73 (m, CH_2), 1.57–1.22 (m, CH_2), 0.93–0.83 (m, CH_3), 0.52 (s, CH_3 of terminal CH=CHSi$(CH_3)_2$Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.8 (s, C^5 of C_6H_3), 138.9 (s, $C^{1,3}$ of C_6H_3), 136.7 ($C^{1,4}$ of C_6H_4), 128.7, 128.5 (each s, CH=CH), 127.0 (s, $C^{2,3,5,6}$ of C_6H_4), 118.0 (s, C^2 of C_6H_3), 111.7 (s, $C^{4,6}$ of C_6H_3), 94.7 (s, C^1 of C_6H_3 of terminal $C_6H_3IOC_8H_{17}$), 68.1 (s, OCH_2), 31.8, 29.4, 29.3, 29.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3), –2.7 (s, CH_3 of terminal CH=CHSi$(CH_3)_2$Ar).

All-trans 1c. Yellowish green solid. ^{1}H NMR ($CDCl_3$): δ 7.98 (br s, $H^{2,6}$ of C_6H_3-3,5-$(CF_3)_2$ of terminal CH=CHSi$(CH_3)_2$Ar), 7.88 (br s, H^4 of C_6H_3-3,5-$(CF_3)_2$ of terminal CH=CHSi$(CH_3)_2$Ar), 7.70–7.50 (m, 8H, $H^{2,6,2',6'}$ and $H^{3,5,3',5'}$ of $C_{12}H_8$), 7.23–7.00 (m, 5H, $H^{2,4}$ and H^6 of C_6H_3 and 2 × CH=CH), 6.57 (d, J = 18.8 Hz, CH=CH of terminal CH=CHSi$(CH_3)_2$Ar), 4.07 (t, J = 6.4 Hz, OCH_2), 3.97 (t, J = 6.4 Hz, OCH_2 of terminal $C_6H_3IOC_8H_{17}$), 1.89–1.75 (br, 2H, CH_2), 1.56–1.25 (br, 10H, CH_2), 0.94–0.87 (br, 3H, CH_3), 0.53 (s, CH_3 of terminal CH=CHSi$(CH_3)_2$Ar). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.9, 159.8 (each s, C^5 of C_6H_3 and C^3 of C_6H_3 of terminal $C_6H_3IOC_8H_{17}$), 139.7, 138.9, 136.3 (each s, $C^{1,1'}$ and $C^{4,4'}$ of $C_{12}H_8$ and $C^{1,5}$ of C_6H_3), 128.6 (br s, CH=CH), 127.0 (br s, $C^{2,6,2',6'}$ and $C^{3,5,3',5'}$ of C_8H_{12}), 118.1 (s, C^2 of C_6H_3), 111.7 (s, $C^{4,6}$ of C_6H_3), 94.7 (s, C^1 of C_6H_3 of terminal $C_6H_3IOC_8H_{17}$), 68.1 (s, OCH_2), 31.9, 29.4, 29.3, 26.2, 22.7 (each s, CH_2), 14.2 (s, CH_3), –2.7 (s, CH_3 of terminal CH=CHSi$(CH_3)_2$Ar).

Synthesis of Model Compounds. (a) (*Z*)-1-octyloxy-3-styrylbenzene ((*Z*)-2).



This compound was prepared by a three-step procedure. (i) To a solution of *m*-bromophenol (**14**; 5.50 g, 31.8 mmol) and 1-bromooctane (9.21 g, 47.7 mmol) in DMF (32 mL) was added K_2CO_3 (11.0 g, 79.5 mmol). The mixture was stirred at 60 °C for 3 h. After cooling to room temperature, water (100 mL) was added, and the mixture was extracted with Et_2O (4 × 100 mL). The combined extracts were washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, evaporated under reduced pressure, and then purified by flash column chromatography (SiO_2, hexane), giving 1-bromo-3-octyloxybenzene (**15**) as a colorless oil (8.08 g, 89% yield). ^{1}H NMR ($CDCl_3$): δ 7.11 (t, J = 8.2 Hz, 1H, H^5 of Ar), 7.07–7.02 (m, 2H, $H^{2,6}$ of Ar), 6.81 (ddd, J = 8.1, 2.3, 1.0 Hz, 1H, H^4 of Ar), 3.92 (t, J = 6.5 Hz, 2H, OCH_2), 1.81–1.72 (m, 2H, CH_2), 1.48–1.22 (several m, 10H, CH_2), 0.92–0.86 (m, 2H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 159.9 (s, C^3 of Ar), 130.4 (s, C^5 of Ar), 123.5 (s, C^6 of Ar), 122.8 (s, C^1 of Ar), 117.7 (s, C^2 of Ar), 113.5 (s, C^4 of Ar), 68.2 (s, OCH_2), 31.8, 29.3, 29.2, 29.1, 26.0, 22.7 (each s, CH_2), 14.1 (s, CH_3). MS, *m*/*z* (relative intensity, %): 286 (M^+ + 1, 5), 284 (M^+ – 1, 5), 174 (50), 172 (52), 76 (6), 71 (15), 70 (11), 69 (11), 57 (36), 56 (13), 55 (32), 43 (84), 42 (17), 41 (100). Anal. Calcd. for $C_{14}H_{21}BrO$: C, 58.95; H, 7.42. Found: C, 58.55; H, 7.42.

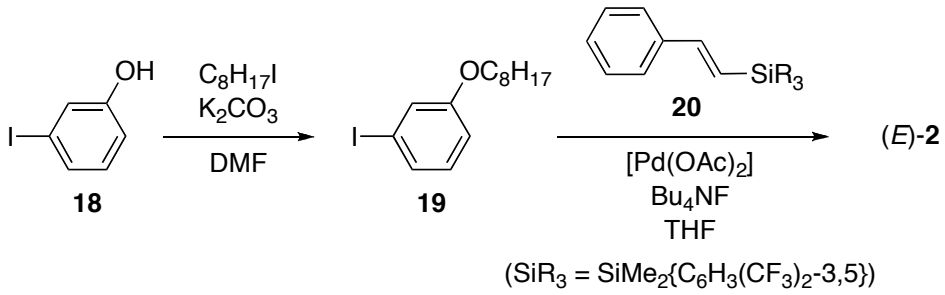
(ii) To a solution of **15** (3.99 g, 14.0 mmol) in THF (70 mL) was added dropwise a 1.59 M solution of *n*-BuLi in hexane (9.2 mL, 15 mmol) at –78 °C. After the mixture was stirred

at this temperature for 1.5 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.20 g, 28.0 mmol) was slowly added. The solution was stirred at –78 °C for 1 h and then at room temperature for 7 h. Water (100 mL) was added, and the mixture was extracted with diethyl ether (4 × 100 mL). The combined extracts were washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, evaporated under reduced pressure, and then purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2 (5/1, 1% Et_3N)), giving 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-octyloxybenzene (**16**) as a colorless oil (3.58 g, 77% yield). ^{1}H NMR ($CDCl_3$): δ 7.38 (d, J = 7.1 Hz, 1H, H^6 of Ar), 7.32 (d, J = 2.5 Hz, 1H, H^2 of Ar), 7.28 (t, J = 8.2 Hz, 1H, H^5 of Ar), 7.00 (ddd, J = 8.2, 2.7, 0.9 Hz, 1H, H^4 of Ar), 3.98 (t, J = 6.5 Hz, 2H, OCH_2), 1.81–1.72 (m, 2H, CH_2), 1.51–1.23 (several m, 10H, CH_2), 1.34 (s, 12H, $C(CH_3)_2$) 0.91–0.87 (m, 2H, CH_3). ^{13}C{^{1}H}NMR ($CDCl_3$): δ 158.6 (s, C^3 of Ar), 128.9 (s, C^5 of Ar), 126.9 (s, C^6 of Ar), 119.6 (s, C^2 of Ar), 118.2 (s, C^4 of Ar), 83.8 (s, $C(CH_3)_2$), 67.9 (s, OCH_2), 31.8, 29.4, 29.3, 26.1 (each s, CH_2), 24.9 (s, $C(CH_3)_2$), 22.7 (s, CH_2), 14.1 (s, CH_3). The ^{13}C signal of C^1 of Ar was obscure due to coupling with quadrupolar ^{11}B nucleus. MS, *m*/*z* (relative intensity, %): 333 (M^+ + 1, 3), 332 (M^+, 13), 220 (24), 219 (8), 205 (19), 135 (13), 134 (86), 133 (5), 121 (16), 120 (19), 83 (12), 69 (15), 59 (11), 57 (32), 55 (36), 43 (100), 42 (24), 41 (99). Anal. Calcd. for $C_{20}H_{33}BO_3$: C, 72.29; H, 10.01. Found: C, 72.25; H, 9.95.

(iii) To a solution of (*Z*)-styryl bromide (**17**; (*Z*) > 99%, 39.5 mg, 0.216 mmol), **16** (68.2 mg, 0.205 mmol), and Bu_4NBr (69.6 mg, 0.216 mmol) in toluene (1.1 mL) were added [$Pd(PPh_3)_4$] (2.5 mg, 2.2 μmol) and 3.0 M aqueous KOH (0.22 mL, 0.65 mmol). The mixture was stirred at 80 °C for 3 h in the dark. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2 (10/1)), giving (*Z*)-**2** ((*E*)/(*Z*) < 1/99) as a colorless oil (62.5 mg, 99% yield). ^{1}H NMR ($CDCl_3$): δ 7.28–7.09 (m, 6H, Ph and H^5 of C_6H_4OR), 6.81 (d, J = 7.6 Hz, 1H, H^6 of C_6H_4OR), 6.77 (s, 1H, H^2 of C_6H_4OR), 6.73 (dd, J = 8.1, 2.4 Hz, 1H, H^4 of C_6H_4OR), 6.60, 6.56 (each d, J = 12.3 Hz, 2H, CH=CH), 3.77 (t, J = 6.6 Hz, 2H, OCH_2), 1.72–1.63 (m, 2H, CH_2), 1.43–1.23 (several m, 10H, CH_2), 0.92–0.87 (m, 3H, CH_3). ^{13}C{^{1}H}NMR ($CDCl_3$): δ 158.9 (s, C^1 of C_6H_4OR), 138.5 (s,

C^3 of C_6H_4OR), 137.3 (s, C^1 of Ph), 130.3, 130.3 (each s, CH=CH), 129.2 (s, C^5 of C_6H_4OR), 128.9, 128.2 (each s, $C^{2,6}$ and $C^{3,5}$ of Ph), 127.1 (s, C^4 of Ph), 121.3 (s, C^6 of C_6H_4OR), 114.3, 114.0 (each s, C^2 and C^4 of C_6H_4OR), 67.8 (s, OCH_2), 31.8, 29.3, 29.3, 29.2, 26.0, 22.7 (each s, CH_2), 14.1 (s, CH_3). MS, *m*/*z* (relative intensity, %): 309 (M^+ + 1, 9), 308 (M^+, 36), 197 (11), 196 (73), 195 (42), 181 (14), 179 (18), 178 (24), 177 (14), 167 (19), 166 (10), 165 (22), 152 (15), 57 (22), 55 (25), 43 (85), 42 (10), 41 (100). Anal. Calcd. for $C_{20}H_{28}O$: C, 85.66; H, 9.15. Found: C, 85.79; H, 9.30.

(b) (*E*)-1-octyloxy-3-styrylbenzene ((*E*)-2).

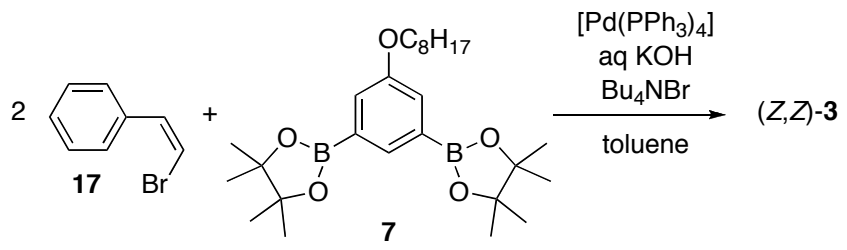


This compound was prepared by a two-step procedure. (i) To a solution of *m*-iodophenol (**18**; 3.02 g, 13.7 mmol) and 1-iodoooctane (3.97 g, 20.6 mmol) in DMF (14 mL) was added K_2CO_3 (4.74 g, 34.3 mmol). The mixture was stirred at 60 °C for 4 h. After cooling to room temperature, water (100 mL) was added, and the mixture was extracted with Et_2O (4 × 100 mL). The combined extracts were washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, evaporated under reduced pressure, and then purified by flash column chromatography (SiO_2, hexane), giving 1-iodo-3-octyloxybenzene (**19**) as a colorless oil (4.47 g, 98% yield). ^{1}H NMR ($CDCl_3$): δ 7.27–7.22 (m, 2H, $H^{2,6}$ of Ar), 6.97 (t, *J* = 8.2 Hz, 1H, H^5 of Ar), 6.87–6.82 (m, 1H, H^4 of Ar), 3.91 (t, *J* = 6.5 Hz, 2H, OCH_2), 1.81–1.72 (m, 2H, CH_2), 1.48–1.22 (m, 10H, CH_2), 0.92–0.86 (m, 2H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 159.7 (s, C^3 of Ar), 130.7 (s, C^5 of Ar), 129.6 (s, C^6 of Ar), 123.6 (s, C^2 of Ar), 114.2 (s, C^4 of Ar), 94.4 (s, C^1 of Ar), 68.2 (s, OCH_2), 31.8, 29.3, 29.2, 29.1, 26.0, 22.7 (each s, CH_2), 14.1 (s, CH_3). MS, m/z (relative intensity, %): 332 (M^+, 11), 220 (71), 93 (11), 76 (13), 71 (12), 69

(11), 65 (14), 64 (10), 57 (33), 55 (31). 43 (79), 41 (100). Anal. Calcd. for $C_{14}H_{21}IO$: C, 50.61; H, 6.37. Found: C, 50.65; H, 6.47.

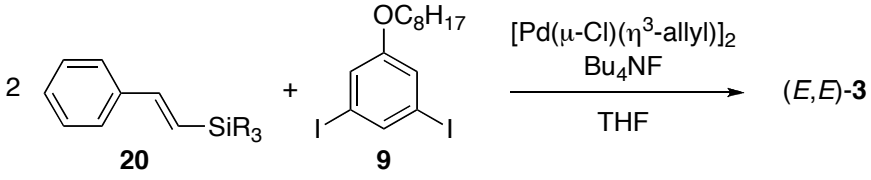
(ii) To a solution of (*E*)-[2-{(3,5-bis(trifluoromethyl)phenyl)dimethylsilyl}ethenyl]-benzene (**20**; (*E*) > 99%, 36.5 mg, 0.0975 mmol) and **19** (34.1 mg, 0.103 mmol) in THF (1 mL) were added [$Pd(OAc)_2$] (2.3 mg, 10 μmol) and 1.0 M solution of $Bu_4NF{\cdot}3H_2O$ in THF (0.10 mL, 0.10 mmol). The mixture was stirred at room temperature for 1 h. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2 (10/1)), giving (*E*)-**2** ((*E*)/(*Z*) > 99/1) as a white solid (27.1 mg, 90% yield). Mp: 33 °C. ^{1}H NMR ($CDCl_3$): δ 7.51 (d, *J* = 7.5 Hz, 2H, $H^{2,6}$ of Ph), 7.36 (t, *J* = 7.5 Hz, 2H, $H^{3,5}$ of Ph), 7.29–7.23 (m, 2H, H^4 of Ph and H^5 of C_6H_4OR), 7.11, 7.07 (each d, *J* = 16.4 Hz, 2H, CH=CH), 7.11–7.07 (m, 1H, H^4 of C_6H_4OR), 7.05 (s, 1H, H^2 of C_6H_4OR), 6.81 (dd, *J* = 8.2, 2,4 Hz, 1H, H^6 of C_6H_4OR), 4.00 (t, *J* = 6.5 Hz, 2H, OCH_2), 1.85–1.75 (m, 2H, CH_2), 1.52–1.20 (several m, 10H, CH_2), 0.93–0.84 (m, 3H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 159.5 (s, C^1 of C_6H_4OR), 138.7 (s, C^3 of C_6H_4OR), 137.3 (s, C^1 of Ph), 129.6 (s, C^5 of C_6H_4OR), 128.9 (s, CH=CH), 128.7 (s, CH=CH), 127.6 (s, C^4 of Ph), 128.7, 126.5 (each s, $C^{2,6}$ and $C^{3,5}$ of Ph), 119.1 (s, C^6 of C_6H_4OR), 113.8, 112.3 (each s, C^2 and C^4 of C_6H_4OR), 68.0 (s, OCH_2), 31.8, 29.4, 29.3, 29.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3). MS, *m*/*z* (relative intensity, %): 309 (M^+ + 1, 7), 308 (M^+, 28), 197 (9), 196 (60), 195 (33), 181 (11), 179 (16), 178 (19), 177 (11), 167 (17), 166 (8), 165 (18), 152 (12), 57 (20), 55 (25), 43 (84), 42 (11), 41 (100). Anal. Calcd. for $C_{20}H_{28}O$: C, 85.66; H, 9.15. Found: C, 85.30; H, 9.24.

(c) (*Z*,*Z*)-1,3-distyryl-5-octyloxybenzene ((*Z*,*Z*)-3).



To a solution of **17** (88.9 mg, 0.486 mmol), **7** (101 mg, 0.221 mmol), and Bu_4NBr (71.2 mg, 0.221 mmol) in toluene (1.1 mL) were added [$Pd(PPh_3)_4$] (12.8 mg, 11.0 μmol) and 3.0 M aqueous KOH (0.22 mL, 0.66 mmol). The mixture was stirred at 80 °C for 24 h in the dark. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2 (10/1)) and then recycle GPC, giving (*Z*,*Z*)-**3** ((*Z*,*Z*) > 99%) as a yellow oil (64.8 mg, 71% yield). ^{1}H NMR ($CDCl_3$): δ 7.26–7.17 (m, 10H, Ph), 6.73 (s, 1H, H^4 of C_6H_3), 6.62 (s, 2H, $H^{2,6}$ of C_6H_3), 6.54 (d, J = 12.2 Hz, 2H, CH=CH), 6.45 (d, J = 12.2 Hz, 2H, CH=CH), 3.59 (t, J = 6.6 Hz, 2H, OCH_2), 1.62–1.54 (m, 2H, CH_2), 1.42–1.18 (several m, 10H, CH_2), 0.93–0.86 (m, 3H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 158.7 (s, C^1 of C_6H_3), 138.4 ($C^{3,5}$ of C_6H_3), 137.2 (s, C^1 of Ph), 130.4, 130.0 (each s, CH=CH), 128.9 ($C^{3,5}$ of Ph), 128.1 (s, $C^{2,6}$ of Ph), 127.1 (s, C^4 of Ph), 122.0 (s, C^4 of C_6H_3), 113.8 (s, $C^{2,6}$ of C_6H_3), 67.7 (s, OCH_2), 31.8, 29.2, 29.2, 29.0, 25.9, 22.7 (each s, CH_2), 14.1 (s, CH_3). MS, *m*/*z* (relative intensity, %): 412 (M^+ + 2, 6), 411 (M^+ + 1, 31), 410 (M^+, 100), 299 (13), 298 (52), 297 (10), 279 (12), 219 (16), 207 (28), 203 (11), 179 (12), 165 (15), 141 (12), 115 (10), 91 (38), 69 (10), 57 (16), 55 (15). Anal. Calcd. for $C_{30}H_{34}O$: C, 87.76; H, 8.35. Found: C, 87.57; H, 8.37.

(d) (*E*,*E*)-1,3-distyryl-5-octyloxybenzene ((*E*,*E*)-3).

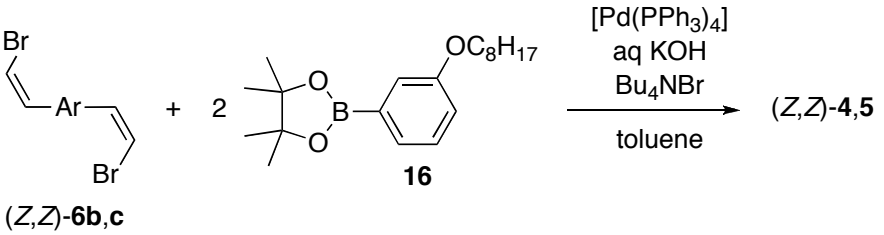


(SiR_3 = $SiMe_2\{C_6H_3(CF_3)_2$-3,5$\}$)

To a solution of (*E*)-**20** (137 mg, 0.366 mmol) and **9** (76.2 mg, 0.166 mmol) in THF (1.7 mL) were added [$Pd(\mu$-Cl)(η^3-allyl)]$_2$ (3.0 mg, 8.3 μmol) and a 1.0 M solution of $Bu_4NF{\cdot}3H_2O$ in THF (0.37 mL, 0.37 mmol). The mixture was stirred at room temperature for 24 h. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2 (10/3)) and then recycle GPC, giving (*E*,*E*)-**3** ((*E*,*E*) >

99%) as a white solid (33.8 mg, 50% yield). Mp: 53–54 °C. ^{1}H NMR ($CDCl_3$): δ 7.53 (d, J = 7.5 Hz, 4H, $H^{2,6}$ of Ph), 7.37 (t, J = 7.5 Hz, 4H, $H^{3,5}$ of Ph), 7.27 (t, J = 7.3 Hz, 2H, H^4 of Ph), 7.25 (s, 1H, H^4 of C_6H_3), 7.15 (d, J = 16.3 Hz, 2H, CH=CH), 7.09 (d, J = 16.3 Hz, 2H, CH=CH), 6.98 (s, 2H, $H^{2,6}$ of C_6H_3), 4.05 (t, J = 6.6 Hz, 2H, OCH_2), 1.87–1.79 (m, 2H, CH_2), 1.54–1.24 (several m, 10H, CH_2), 0.93–0.87 (m, 3H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 159.8 (s, C^1 of C_6H_3), 138.9 ($C^{3,5}$ of C_6H_3), 137.2 (s, C^1 of Ph), 129.2, 128.5 (each s, CH=CH), 127.7 (s, C^4 of Ph), 128.7 (s, $C^{3,5}$ of Ph), 126.6 (s, $C^{2,6}$ of Ph), 117.9 (s, C^4 of C_6H_3), 111.7 (s, $C^{2,6}$ of C_6H_3), 68.1 (s, OCH_2), 31.8, 29.4, 29.4, 29.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd. for $C_{30}H_{34}O$: C, 87.76; H, 8.35. Found: C, 87.51; H, 8.39.

(e) (*Z*,*Z*)-Bis(3-octyloxystyryl)arenes ((*Z*,*Z*)-4 and 5).



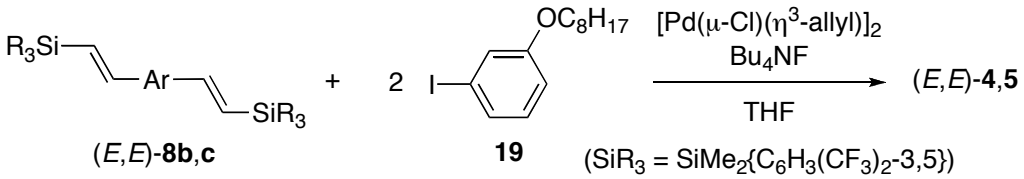
A typical procedure is reported for (*Z*,*Z*)-**4**. To a solution of (*Z*,*Z*)-**6b** ((*E*)/(*Z*) < 1/99) (109 mg, 0.300 mmol), **16** (219 mg, 0.660 mmol), and Bu_4NBr (96.7 mg, 0.300 mmol) in toluene (1.5 mL) were added [$Pd(PPh_3)_4$] (17.3 mg, 15.0 μmol) and 3.0 M aqueous KOH (0.30 mL, 0.90 mmol). The mixture was stirred at 80 °C for 24 h in the dark. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2 (8/1)) and then recycle GPC, giving the title compound ((*Z*,*Z*) > 99%) as a pale yellow oil (124 mg, 91% yield). (*Z*,*Z*)-**5** was similarly synthesized using (*Z*,*Z*)-**6c** ((*Z*,*Z*) > 99%) in 84% yield.

***(Z,Z)*-4.** Pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.13 (s, 4H, *p*-phenylene), 7.11 (t, J = 7.9 Hz, 2H, H^5 of C_6H_4OR), 6.82 (d, J = 7.7 Hz, 2H, H^6 of C_6H_4OR), 6.79 (s, 2H, H^2 of C_6H_4OR), 6.73 (dd, J = 8.2, 2.4 Hz, 2H, H^4 of C_6H_4OR), 6.55, 6.51 (each d, J = 12.4 Hz, 4H, CH=CH), 3.81 (t, J = 6.6 Hz, 4H, OCH_2), 1.74–1.66 (m, 4H, CH_2), 1.44–1.22 (several m, 20H,

CH_2), 0.92–0.86 (m, 6H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 159.0 (s, C^3 of C_6H_4OR), 138.6 (s, C^1 of Ar), 136.0 (s, C^1 of *p*-phenylene), 130.2, 130.0 (each s, CH=CH), 129.1 (s, C^5 of C_6H_4OR), 128.8 (s, $C^{2,3,5,6}$ of *p*-phenylene), 121.3 (s, C^6 of C_6H_4OR), 114.5, 113.8 (each s, C^2 and C^4 of C_6H_4OR), 67.8 (s, OCH_2), 31.8, 29.3, 29.2, 29.2, 26.0, 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd. for $C_{38}H_{50}O_2$: C, 84.71; H, 9.35. Found: C, 84.43; H, 9.36.

(*Z*,*Z*)-5. Pale yellow oil. ^1H NMR ($CDCl_3$): δ 7.45, 7.31 (each d, *J* = 8.2 Hz, 8H, $C_{12}H_8$), 7.13 (t, *J* = 7.8 Hz, H^5 of C_6H_4OR), 6.86 (d, *J* = 7.6 Hz, 2H, H^6 of C_6H_4OR), 6.82 (s, 2H, H^2 of C_6H_4OR), 6.75 (dd, *J* = 8.2, 2.4 Hz, 2H, H^4 of C_6H_4OR), 6.59 (s, 4H, CH=CH), 3.80 (t, *J* = 6.6 Hz, 4H, OCH_2), 1.73–1.64 (m, 4H, CH_2), 1.42–1.19 (several m, 20H, CH_2), 0.91–0.84 (m, 6H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 159.0 (s, C^3 of C_6H_4OR), 139.2, (s, $C_{12}H_8$) 138.5 (s, C^1 of C_6H_4OR), 136.2 (s, $C_{12}H_8$), 130.4, 129.8 (each s, CH=CH), 129.8 (s, $C_{12}H_8$), 129.2 (s, C^5 of C_6H_4OR), 126.5 (s, $C_{12}H_8$), 121.2 (s, C^6 of C_6H_4OR), 114.4, 113.8 (each s, C^2 and C^4 of C_6H_4OR), 67.8 (s, OCH_2), 31.8, 29.3, 29.2, 29.2, 26.0, 22.6 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd. for $C_{44}H_{54}O_2$: C, 85.94; H, 8.85. Found: C, 85.87; H, 8.87.

(f) (*E*,*E*)-Bis(3-octyloxystyryl)arenes ((*E*,*E*)-4 and 5).



A typical procedure is reported for (*E*,*E*)-**4**. To a solution of (*E*,*E*)-**8b** ((*E*)/(*Z*) > 99/1) (268 mg, 0.400 mmol) and **19** (292 mg, 0.880 mmol) in THF (4 mL) were added [Pd(μ-Cl)(η^3-allyl)]$_2$ (14.6 mg, 40.0 μmol) and 1.0 M solution of $Bu_4NF{\cdot}3H_2O$ in THF (0.80 mL, 0.80 mmol). The mixture was stirred at room temperature for 72 h. The solution was concentrated to dryness, and the residue was purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2 (4/1)), giving (*E*,*E*)-**4** ((*E*,*E*) > 99%) as a white solid (109 mg, 52% yield). (*E*,*E*)-**5** was similarly synthesized using (*E*,*E*)-**8c** ((*E*,*E*) > 99%) in 51% yield.

(*E*,*E*)-4. Pale yellow solid. Mp: 112 °C. ^{1}H NMR ($CDCl_3$): δ 7.50 (s, 4H, *p*-phenylene), 7.26 (t, *J* = 7.9 Hz, 2H, H^5 of Ar), 7.12–7.08 (m, 6H, H^6 of Ar and 2 × CH=CH), 7.06 (s, 2H, H^2 of Ar), 6.81 (dd, *J* = 7.8, 2.0 Hz, 2H, H^4 of Ar), 4.00 (t, *J* = 6.6 Hz, 4H, OCH_2), 1.85–1.76 (m, 4H, CH_2), 1.52–1.25 (several m, 20H, CH_2), 0.93–0.87 (m, 6H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 159.5 (s, C^3 of Ar), 138.7 (s, C^1 of Ar), 136.7 (s, $C^{1,4}$ of *p*-phenylene), 129.6 (s, C^5 of Ar), 128.6, 128.5 (each s, CH=CH), 126.9 (s, $C^{2,3,5,6}$ of *p*-phenylene), 119.1 (s, C^4 of Ar), 113.9, 112.3 (each s, C^2 and C^6 of Ar), 68.0 (s, OCH_2), 31.8, 29.4, 29.4, 29.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd. for $C_{38}H_{50}O_2$: C, 84.71; H, 9.35. Found: C, 84.45; H, 9.19.

(*E*,*E*)-5. Pale yellow solid. Mp: 182 °C. ^{1}H NMR ($CDCl_3$): δ 7.64, 7.59 (each d, *J* = 8.4 Hz, 8H, $C_{12}H_8$), 7.27 (t, *J* = 7.9 Hz, 2H, H^5 of Ar), 7.15–7.10 (m, 6H, H^6 of Ar and 2 × CH=CH), 7.08 (s, 2H, H^2 of Ar), 6.82 (dd, *J* = 8.1, 2.3 Hz, 2H, H^4 of Ar), 4.01 (t, *J* = 6.6 Hz, 4H, OCH_2), 1.86–1.77 (m, 4H, CH_2), 1.53–1.25 (several m, 20H, CH_2), 0.93–0.87 (m, 6H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 159.5 (s, C^3 of Ar), 139.8 (s, $C_{12}H_8$), 138.7 (s, C^1 of Ar), 136.4 (s, $C_{12}H_8$), 129.6 (s, C^5 of Ar), 128.8, 128.4 (each s, CH=CH), 127.1, 127.0 (each s, $C_{12}H_8$), 119.2 (s, C^4 of Ar), 113.9, 112.4 (each s, C^2 and C^6 of Ar), 68.0 (s, OCH_2), 31.9, 29.4, 29.4, 29.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd. for $C_{44}H_{54}O_2$: C, 85.94; H, 8.85. Found: C, 85.52; H, 8.86.

Photoisomerization in Solution. A sample solution in benzene (4 mg L^{-1}) was prepared in a quartz cell. Nitrogen gas was bubbled through the solution at room temperature for 5 min. The sample was irradiated with a Xe lamp (λ_{max} = 365 nm, 0.87 mW cm^{-2}), and the photoisomerization was monitored by UV-vis absorption spectroscopy.

Photoisomerization of PmPVs in Thin Films. A solution of PmPV in $CHCl_3$ (2.0 wt%) was passed through a syringe filter (DISMIC-13 JP, PTFE 0.50 μm, Hydrophobic; ADVANTEC). A thin film of PmPV was prepared by spin-coating on a quartz plate (1 cm^2); the filtrate (50 μL) was dropped on a plate, and the plate was accelerated to 1200 rpm rotation for 2 s, kept at this rate for 10 s, and then rotated at 2000 rpm for 60 s. After dried under

vacuum at room temperature for 30 min, the film was placed in a quartz cell under a nitrogen atmosphere, and analyzed by UV-vis absorption spectroscopy. Next, the film was placed in a stainless-steel holder with a quartz window, irradiated by a Xe lamp (λ_{max} = 365 nm, 21.0 mW cm^{-2}), and the photoisomerization was monitored by UV-vis absorption spectroscopy. The photo-irradiated film was rinsed twice in $CHCl_3$ (each 3 mL) with light shaking, dried under vacuum at room temperature, and examined by UV-vis absorption spectroscopy.

References and Notes

(1) (a) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Umeda, K.; Akamatsu, K.; Tsuruoka, T.; Nawafune, H.; Ozawa, F. *J. Am. Chem. Soc.* **2005**, *127*, 4350–4353. (b) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Fukuse, Y.; Wakioka, M.; Ozawa, F. *Macromolecules* **2006**, *39*, 2039–2048. (c) Katayama, H.; Ozawa, F.; Matsumiya, Y.; Watanabe, H. *Polym. J.* **2006**, *38*, 184–189.

(2) (a) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415–436. (b) Meier, H. *Angew. Chem., Int. Ed. Eng.* **1992**, *31*, 1399–1420. (c) Arai, T.; Tokumaru, K. *Chem. Rev.* **1993**, *93*, 23–39.

(3) (a) Katayama, H.; Nagao, M.; Ozawa, F.; Ikegami, M.; Arai, T. *J. Org. Chem.* **2006**, *71*, 2699–2705. (b) Ikegami, M.; Nagao, M.; Katayama, H.; Ozawa, F.; Arai, T. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1833–1835.

(4) (a) Doi, S.; Osada, T.; Tsuchida, Y.; Noguchi, T.; Ohnishi, T. *Synth. Met.* **1997**, *85*, 1281–1282. (b) Davey, A. P.; Drury, A.; Maier, S.; Byrne, H. J.; Blau, W. J. *Synth. Met.* **1999**, *103*, 2478–2479. (c) Ahn, T.; Jang, M. S.; Shim, H.-K.; Hwang, D.-H.; Zyung, T. *Macromolecules* **1999**, 32, 3279–3285. (d) Pang, Y.; Li, J.; Hu, B.; Karasz, F. E. *Macromolecules* **1999**, *32*, 3946–3950. (e) Schlick, H.; Stelzer, F.; Tasch, S.; Leising, G. *J. Mol. Cat. A: Chem.* **2000**, *160*, 71–84. (f) Schlick, H.; Stelzer, F.; Meghdadi, F.; Leising, G. *Synth. Met.* **2001**, *119*, 529–530. (g) Liao, L.; Pang, Y.; Ding, L.; Karasz, F. E. *Macromolecules* **2001**, *34*, 6756–6760. (h) Liao, L.; Pang, Y.; Ding, L.; Karasz, F. E.

Macromolecules **2001**, *34*, 7300–7305. (i) Drury, A.; Maier, S.; Ruether, M.; Blau, W. J. *J. Mater. Chem.* **2003**, *13*, 485–490.

(5) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483. (b) Miyaura N. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A.; Diederich, F. Eds; WILEY-VCH, Weinheim, Germany, 2004; Chapter 2.

(6) Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet. Chem.* **2003**, *676*, 49–54.

(7) (a) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845–853. (b) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471–1478. (c) Hiyama T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F.; Stang, P. J. Eds; WILEY-VCH, Weinheim, Germany, 1998; Chapter 10. (d) Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A.; Diederich, F. Eds; WILEY-VCH, Weinheim, Germany, 2004; Chapter 4.

(8) The OCH_2 proton signals appear at around δ 3.6 and 4.0 for cis and trans isomers, respectively. The upfield shifts observed for cis isomers are due to the shielding effects of arylene rings as previously reported.[1a,1b,7]

(9) The small signal observed at 3.84–3.70 for all-cis **1a** ((a) in Figure 1A) was assigned to the OCH_2 protons of terminal $C_6H_4OC_8H_{17}$ group, formed by hydrolysis of benzeneboronic acid ester; the chemical shift was in accordance with that of (*Z*)-**2** (δ 3.77).

(10) The absorption intensity gradually decreased upon prolonged irradiation, probably due to the occurrence of side reactions such as [2+2] cycloaddition of vinylene groups: Meier, H.; Kretzschmann, H.; Lang, M.; Frass, W.; Albrecht, C.; Maerz, K. *J. Prakt. Chem.* **1994**, *336*, 297–302.

(11) Coulson, D. R. *Inorg. Synth.* **1971**, *13*, 121–124.

(12) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220–221.

(13) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45–64.

(14) Nagao, M.; Asano, K.; Umeda, K.; Katayama, H.; Ozawa, F. *J. Org. Chem.* **2005**, *70*, 10511–10514.

(15) Larionova, Y. A.; Ponomarev, A. I.; Klebanskii, A. L.; Yuzhelevskii, Y. A.; Zaitsev, N. B.; Bogdanova, V. V. *Zh. Obshch. Khim.* **1971**, *41*, 1256–1263.

(16) Sumiya, K.; Kwak, G.; Sanda, F.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2774–2783.

(17) Kim, S. H.; Wei, H.-X.; Willis, S.; Li, G. *Synth. Commun.* **1999**, *29*, 4179–4185.

(18) Katayama, H.; Taniguchi, K.; Kobayashi, M.; Sagawa, T.; Minami, T.; Ozawa, F. *J. Organomet. Chem.* **2002**, *645*, 192–200.

(19) Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508–7510.

Chapter 3

Reaction of *trans*-[Pd(CH=CHPh)Br($PMePh_2$)$_2$] with Styryl Bromide Affording 1,4-Diphenylbutadiene. An Unexpected Homo-Coupling Process Induced by P–C Reductive Elimination

Abstract

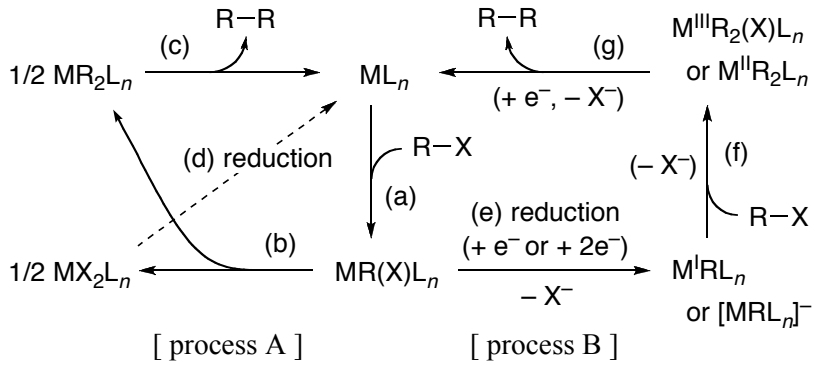
Reaction of (*Z*)-styryl bromide (**1**) with $PhB(OH)_2$ in toluene at 80 °C for 1 h in the presence of [$Pd(PPh_3)_4$] (1.5 mol%) and an aqueous solution of K_2CO_3 (3 equiv) affords (*Z*)-stilbene as the cross-coupling product in 99% yield. On the other hand, the same reaction of the (*E*)-isomer of **1** forms considerable amounts of homo-coupling 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-(*E*)}Br($PMePh_2$)$_2$] ((*E*)-**3**) as a model of the presumed intermediate. Complex (*E*)-**3** reacts with (*E*)-**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=CHP$MePh_2$}Br($PMePh_2$)] (**5**, 8%). The reaction rate shows first-order dependence on the concentration of (*E*)-**3** and **5**, respectively, but is independent of the concentration of (*E*)-**1**. A novel homo-coupling process induced by P–C reductive elimination from (*E*)-**3** giving **5** is proposed.

Introduction

As shown in Chapter 1, Suzuki–Miyaura-type polycondensation of (*Z*,*Z*)-1,4-bis-(2-bromoethenyl)benzene with 2,5-dioctyloxybenzene-1,4-diboronic acid cleanly forms all-cis poly(*p*-phenylenevinylene) (PpPV), which undergoes photo-induced insolubilization in thin films. It has been found that a 2-bromoethenyl group at the polymer end facilitates the photo-induced insolubilization to a notable extent. For further investigation of this phenomenon, the author has tried to synthesize all-trans PpPV bearing a 2-bromoethenyl group by Suzuki–Miyaura-type polycondensation, but (*E*,*E*)-1,4-bis (2-bromoethenyl)benzene has been found to provide a polymer containing a notable amount of butadiene unit in the main chain, resulting from the homo-coupling of alkenyl bromide.[1] Therefore, the author has considered that the mechanistic information about the homo-coupling process should be essential for achieving a highly selective synthesis of all-trans PpPV without structural defects.

Scheme 1 illustrates a schematic view of homo-coupling processes previously reported. The first step is oxidative addition of organic halides (R–X) 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 homo-coupling products (R–R). Process A involves metathesis of [$MR(X)L_n$] to give [MR_2L_n] and [MX_2L_n] (step b).[8] The former forms R–R 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 (Ar–Br) 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 [$Ni^{II}Br_2(PEt_3)_n$].[9] More recently, Osakada and Yamamoto examined metathesis of diamagnetic [MAr(X)(bipy)] complexes (M = Ni, Pd; bipy = 2,2'-bipyridine) in detail and demonstrated high reactivity of cationic $[MAr(bipy)]^+$ species.[10]

Scheme 1

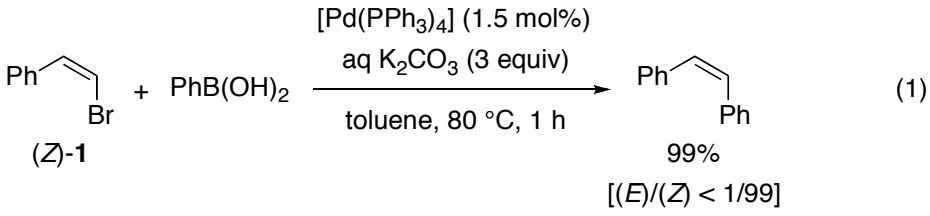


On the other hand, process B involves oxidative addition of R–X to paramagnetic $M^{I}RL_n$ or anionic $[MRL_n]^-$ species generated by chemical or electrochemical reduction of $[MR(X)L_n]$ (step e → step f).[11] The reaction forms $[M^{III}R_2(X)L_n]$ or $[MR_2L_n]$, which reductively eliminates R–R (step g). This type of process was originally proposed for nickel-catalyzed reactions by Colon and Kelsey[11] and expanded to palladium-catalyzed systems by Amatore and Jutand.[12]

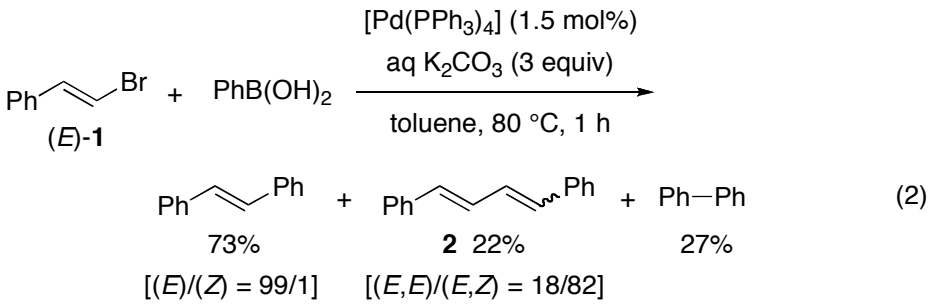
This chapter deals with the homo-coupling process of styryl bromide (**1**) promoted by palladium(0) phosphine complexes. The author has attempted to clarify the following points using a model reaction of isolated *trans*-$[Pd(CH=CHPh)Br(PMePh_2)_2]$ (**3**)[13] with styryl bromide to give 1,4-diphenylbutadiene: (i) the effect of (*E*)/(*Z*) configuration of the styryl group; (ii) the mechanism of the homo-coupling process. It has been found that the butadiene formation proceeds via a novel homo-coupling process induced by P–C reductive elimination from **3** to give $[Pd(\eta^2\text{-}PhCH=CHPMePh_2)Br(PMePh_2)]$ (**5**).[14]

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 homo-coupling 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 homo-coupling process.



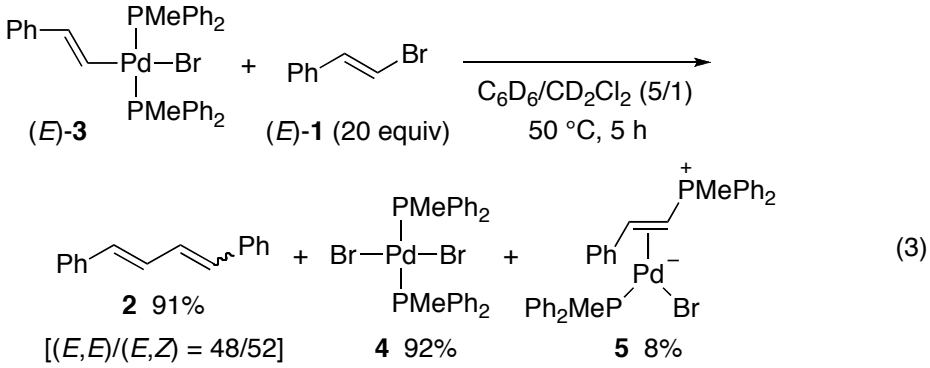
(1)



(2)

Next, the author examined the homo-coupling 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 the 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**).[15] 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-diphenyl-butadiene (**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 towards homo-coupling, and (ii) the occurrence of (*E*)/(*Z*) isomerization of styryl group during the homo-coupling 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.[14,16]



(3)

Kinetic Examination of the Homo-Coupling 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 the other palladium species [Pd{CH=CHPh-(*E*)}(μ-Br)($PMePh_2$)]$_2$ (**6**)[17] 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.[14c]

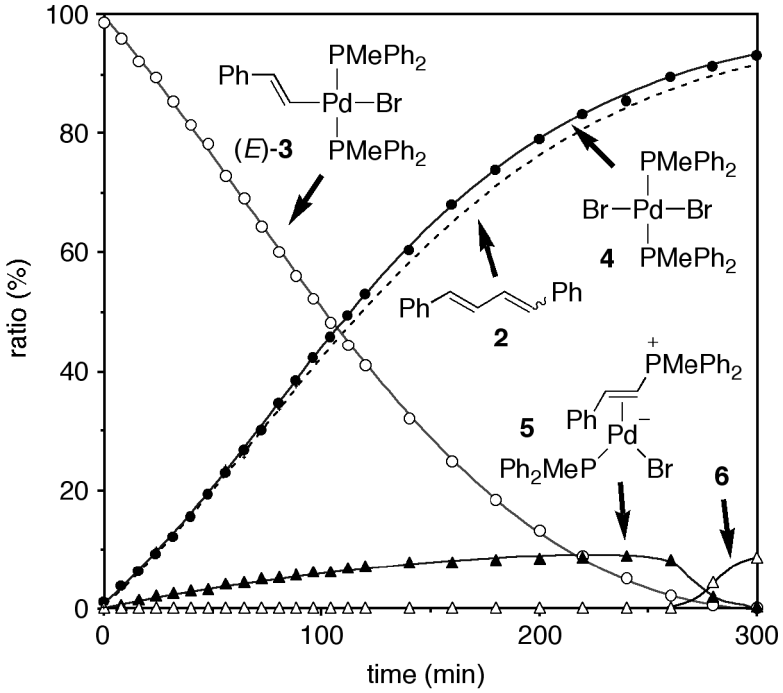


Figure 1. The time-course of the reaction of (*E*)-**3** (50 mM) with (*E*)-**1** (1.0 M) in C_6D_6/CD_2Cl_2 (5/1 = v/v) at 50 °C.

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*)-**3**]$_0$ = 50 mM). Both the yield and the formation rate of **4** are enhanced by addition of **5** to the system ([**5**]$_0$ = 5–15 mM, runs 1–3). Furthermore, the amount of **5** generated from (*E*)-**3** during the reaction clearly decreases as the amount of added **5** increases.[18] It should be noted that the time-yield curves for **4** have a simple form (not *S*-shaped). Actually, the reactions obeyed the 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: $d[\mathbf{4}]/dt = k_2[(E)\text{-}\mathbf{3}][\mathbf{5}]$.

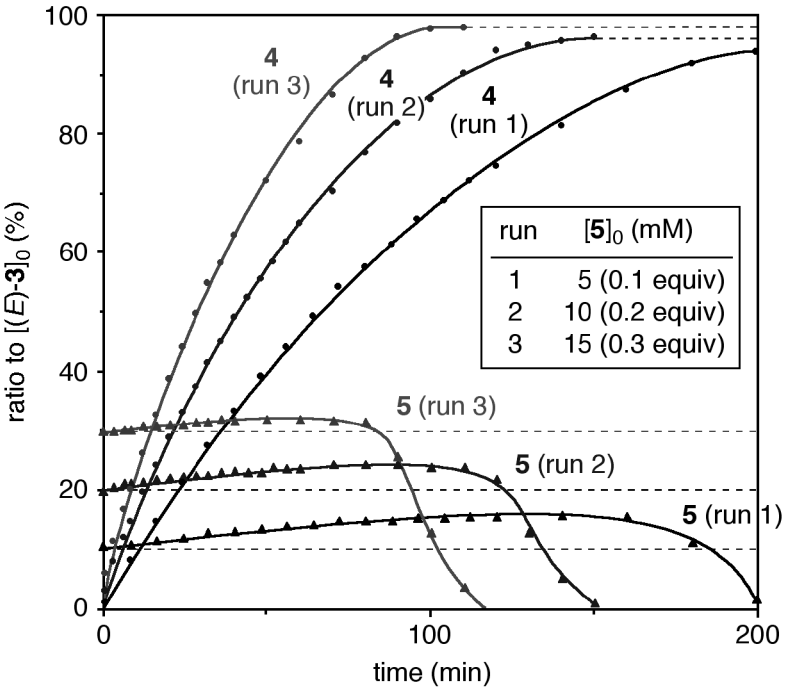


Figure 2. The time-course of the reaction of (*E*)-**3** (50 mM) with (*E*)-**1** (1.0 M) in C_6D_6/CD_2Cl_2 (5/1 = v/v) at 50 °C in the presence of isolated **5**.

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

run	$[\mathbf{5}]_0$ (mM)	$10^4 k_1$ (s^{-1}) [b]	$10^2 k_2$ (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_6 (5/1 = v/v), at 50 °C. [b] Estimated by regression analysis of the kinetic data (up to 63% conversion of (*E*)-**3**) using the following equation: $\ln\{[(E)\text{-}\mathbf{3}]_0/([(E)\text{-}\mathbf{3}]_0 - [\mathbf{4}]_t)\} = k_1 t$. [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] The 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%).

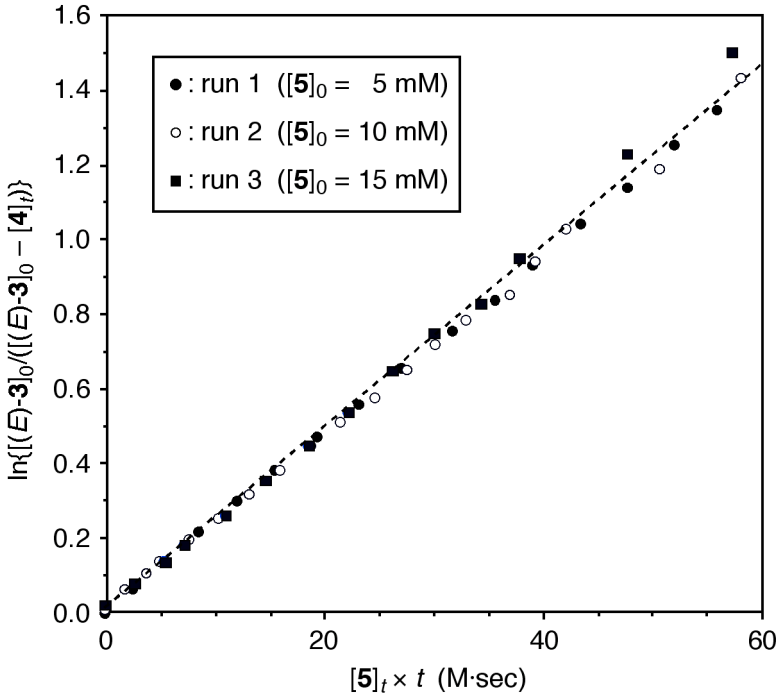


Figure 3. Plot of $\ln\{[(E)\text{-}\mathbf{3}]_0/([(E)\text{-}\mathbf{3}]_0 - [\mathbf{4}]_t)\}$ vs. $([\mathbf{5}]_t \times t)$ for the reactions of Figure 2.

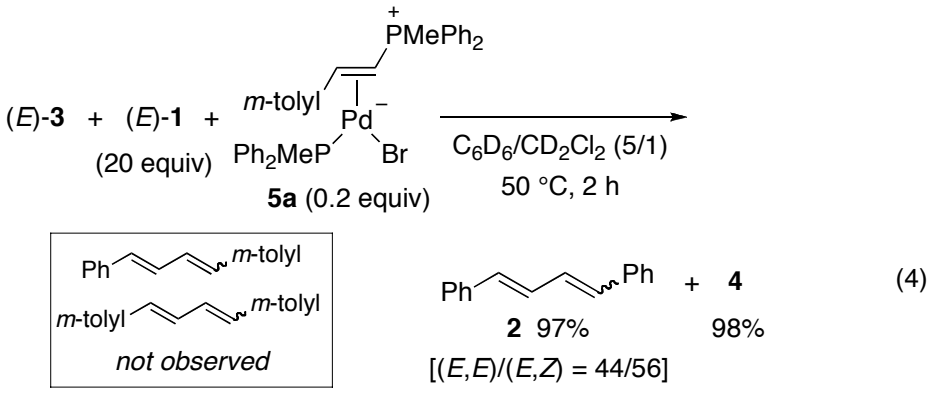
Table 2 compares half-lives of (*E*)-**3** under various conditions. The reaction is highly sensitive to solvent polarity and clearly faster in a polar solvent (runs 1–3; runs 4–5). On the other hand, the reaction rate is less sensitive to the concentration of (*E*)-styryl bromide ((*E*)-**1**) (runs 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, 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 homo-coupling (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.

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

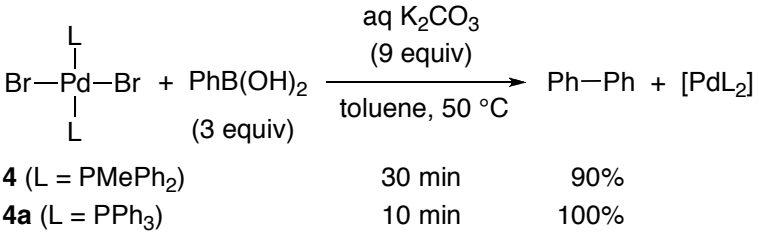
run	$[(E)\text{-}\mathbf{1}]_0$ (M)	solvent	additive	$t_{1/2}$ (min)
1	1.0	C_6D_6	—	200
2	1.0	C_6D_6/CD_2Cl_2 (5/1)	—	100
3	1.0	C_6D_6/CD_2Cl_2 (1/1)	—	48
4	0.50	C_6D_6	—	240
5	0.50	C_6D_6/CD_2Cl_2 (5/1)	—	76
6	1.0	C_6D_6/CD_2Cl_2 (5/1)	$PMePh_2$ (5 mM)	280
7	1.0	C_6D_6/CD_2Cl_2 (5/1)	**7** (1.5 mM)[b]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

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

Labeling Experiment. The kinetic experiments revealed a crucial role of styrylphosphonium complex **5** in the homo-coupling process. In this connection, the reaction of (*E*)-**3** with (*E*)-**1** was examined in the presence of [Pd{η^2-(*E*)-*m*-$MeC_6H_4CH{=}CH$-$PMePh_2$}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.



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)

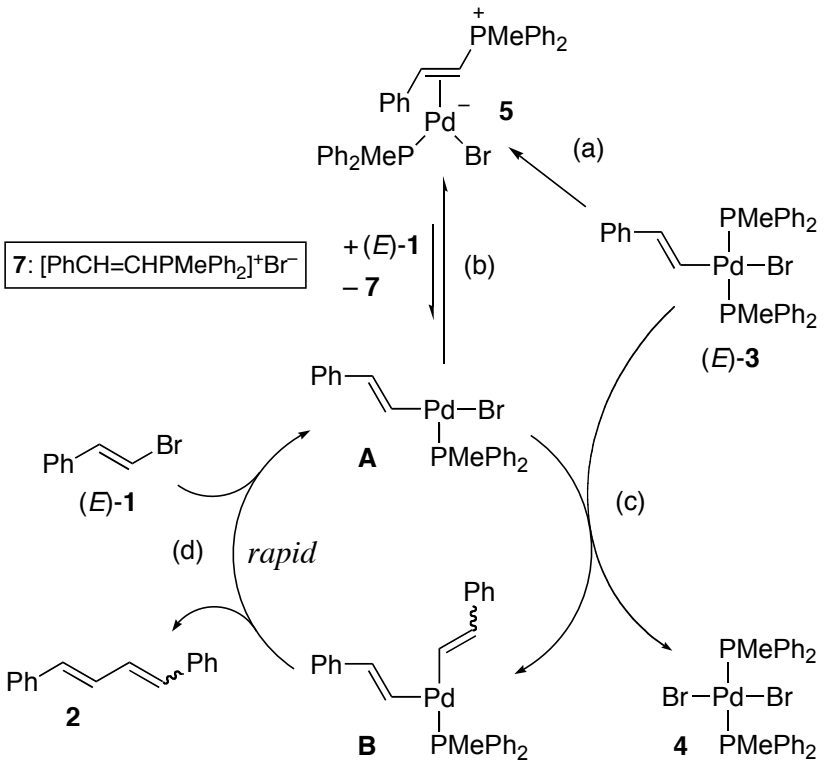
Discussion

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 homo-coupling 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 homo-coupling 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 homo-coupling product **2**. (7) Palladium dibromide (**4** or **4a**) is 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, the author proposes 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.),[19] 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).[20]

Scheme 2

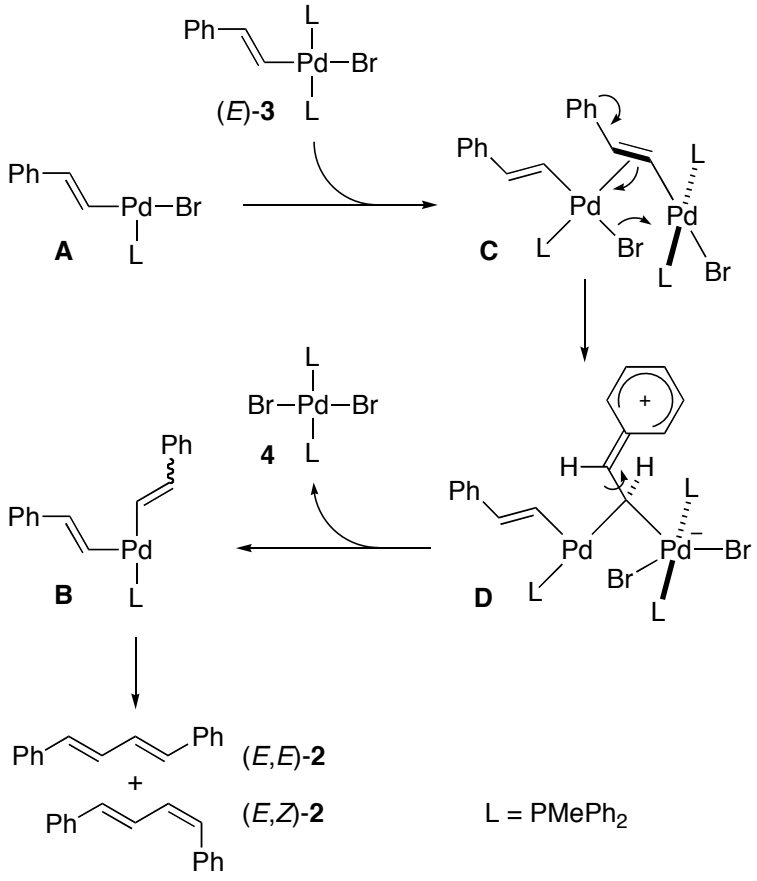


Complex **A** serves as a key intermediate in the production process. Intermolecular exchange of the styryl ligand in **A** and the bromo ligand in (*E*)-**3** forms bis(styryl) complex **B** and dibromo complex **4** (step c). Reductive elimination of **2** from **B**, followed by oxidative addition 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.[13,21]

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 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**.[22] 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

Scheme 3



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.

Conclusions

The author has demonstrated a novel homo-coupling 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 reductive elimination of the styryl and

$PMePh_2$ ligands from (*E*)-**3**, followed by oxidative addition of (*E*)-**1** to resulting styrylphosphonium complex **5**. The author has 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 homo-coupling 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.[12] In contrast, the author 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 previous observations of Ozawa and Yamamoto for the reactions of *trans*-$[PdAr_2L_2]$ with R–X (R = Me, aryl; L = PEt_2Ph), where *trans*-$[PdR(X)L_2]$ formed by oxidative addition of R–X to a palladium(0) species catalyzes the conversion of *trans*-$[PdAr_2L_2]$ and R–X into Ar–R.[23]

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.

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 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.[24] The following compounds were synthesized according to the literature: (*Z*)-styryl bromide ((*Z*)-**1**),[25] $[Pd(PPh_3)_4]$,[26] *trans*-[Pd{CH=CHPh-(*Z*)}Br$(PMePh_2)_2$] ((*Z*)-**3**),[13a] *trans*-$[PdBr_2(PMePh_2)_2]$ (**4**),[27] *trans*-$[PdBr_2(PPh_3)_2]$ (**4a**),[28] $[(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)Pd]$,[29] $[Pd(PMePh_2)_4]$,[30] and $[Pd(dba)_2]$.[31]

Synthesis of *trans*-[Pd{CH=CHPh-(*E*)}Br$(PMePh_2)_2$] ((*E*)-3). $PMePh_2$ (411 mg, 2.05 mmol) was added to a solution of $[(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)Pd]$ (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 $[Pd(PMePh_2)_4]$ (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). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.9 (d, $^3J_{PC}$ = 5 Hz), 134.7 (d, $^4J_{PC}$ = 3 Hz), 133.6 (d, $^2J_{PC}$ = 20 Hz), 132.9 (d, $^3J_{PC}$ = 11 Hz), 131.9 (s), 130.2 (d, $^2J_{PC}$ = 13 Hz), 129.2 (s), 129.1 (s), 119.7 (d, $^1J_{PC}$ = 90 Hz), 106.4 (d, $^1J_{PC}$ = 89 Hz), 10.7 (d, $^1J_{PC}$ = 59 Hz). $^{31}P\{^1H\}$ 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, 1.58 mmol) in toluene (8 mL) in the presence of $[Pd(PMePh_2)_4]$ (71.8 mg, 79.1 μmol) (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). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.2 (d, $^3J_{PC}$ = 4 Hz), 138.9 (s), 134.7 (d, $^4J_{PC}$ = 3 Hz), 133.5 (d, $^2J_{PC}$ = 20 Hz), 132.9 (d, $^3J_{PC}$ = 11 Hz), 132.8 (s), 130.2 (d, *J* = 13 Hz), 129.7 (s), 129.0, (s), 126.4 (s), 119.8 (d, $^1J_{PC}$ = 90 Hz), 105.9 (d, $^1J_{PC}$ = 89 Hz), 21.2 (s), 10.7 (d, $^1J_{PC}$ = 59 Hz). $^{31}P\{^1H\}$ 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-(*E*)-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 $[Pd(dba)_2]$ (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). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 144.8 (d, $^3J_{PC}$ = 11 Hz), 139.3 (d, $^1J_{PC}$ = 28 Hz), 137.0 (d, $^1J_{PC}$ = 29 Hz), 134.9 (d, $^3J_{PC}$ = 10 Hz), 133.5 (s), 134.8 (s), 132.8 (d, $^2J_{PC}$ = 14 Hz), 132.6 (d, $^3J_{PC}$ = 10 Hz), 132.5 (d, $^2J_{PC}$ = 14 Hz), 129.9 (d, $^2J_{PC}$ = 11 Hz), 129.2 (s), 129.1 (d, $^2J_{PC}$ = 12 Hz), 128.9 (d, $^4J_{PC}$ = 1 Hz), 128.7 (s), 128.4 (d, $^3J_{PC}$ = 9 Hz), 128.2 (d, $^3J_{PC}$ = 9 Hz), 127.4 (dd, $^1J_{PC}$ = 73 Hz, $^4J_{PC}$ = 10 Hz), 125.7 (s), 124.9 (s), 124.9 (d, $^1J_{PC}$ = 93 Hz), 59.5 (d, $^2J_{PC}$ = 5 Hz), 28.3 (dd, $^1J_{PC}$ = 81 Hz, $^2J_{PC}$ = 36 Hz), 14.6 (d, $^1J_{PC}$ = 19 Hz), 13.7 (d, $^1J_{PC}$ = 67 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.9 (d, $^3J_{PP}$ = 7 Hz), 6.7 (d, $^3J_{PP}$ = 6 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-(*E*)-*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) (25.1 mg, 16%). Mp: 124–126 °C (dec). ^1H 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). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 144.6 (d, $^3J_{PC}$ = 12 Hz), 139.5 (d, $^1J_{PC}$ = 28 Hz), 138.2 (s), 137.0 (d, $^1J_{PC}$ = 29 Hz), 134.9 (d, $^3J_{PC}$ = 10 Hz), 133.5 (br), 132.8 (d, $^2J_{PC}$ = 14 Hz), 132.5 (d, $^2J_{PC}$ = 14 Hz), 129.9 (d, $^3J_{PC}$ = 11 Hz), 129.2 (s), 129.1 (d, $^3J_{PC}$ = 13 Hz), 128.9 (s), 128.6 (s), 128.5 (d, $^3J_{PC}$ = 9 Hz), 128.2 (d, $^3J_{PC}$ = 9 Hz), 127.4 (dd, $^1J_{PC}$ = 73 Hz, $^4J_{PC}$ = 10 Hz), 126.5 (s), 125.7 (s), 124.8 (d, $^1J_{PC}$ = 93 Hz), 122.6 (s), 59.8 (d, $^2J_{PC}$ = 5 Hz), 28.2 (dd, $^1J_{PC}$ = 82 Hz, $^2J_{PC}$ = 36 Hz), 21.5 (s), 14.6 (d, $^1J_{PC}$ = 19 Hz), 13.7 (d, $^1J_{PC}$ = 66 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.8 (d, $^3J_{PP}$ = 8 Hz), 6.7 (d, $^3J_{PP}$ = 6 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 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 septum and placed in an NMR probe controlled to 50.0 ± 0.1 °C. The reaction was followed at intervals by ^1H 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). $^{31}P\{^1H\}$ 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.

References and Notes

(1) Dehalogenative homo-coupling of aryl and alkenyl halides promoted by nickel[2] and palladium[3] complexes is a useful means of C–C bond formation,[4] especially for the synthesis of π-conjugated polymers.[5] This reaction also takes place quite often as a side reaction of the catalytic cross-coupling of organic halides with organometallic reagents.[6,7]

(2) (a) Semmelhack, M. F.; Helquist, P. M.; Jones, L. D. *J. Am. Chem. Soc.* **1971**, *93*, 5908–5910. (b) Semmelhack, M. F.; Helquist, P. M.; Gorzynski, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 9234–9236. (c) Kende, A. S.; Liebeskind, L.; Braitsch, D. M. *Tetrahedron Lett.* **1975**, 3375–3378. (d) Zembayashi, M.; Tamao, K.; Yoshida, J.; Kumada, M. *Tetrahedron Lett.* **1977**, 4089–4092. (e) Takagi, K.; Hayama, N.; Inokawa, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3691–3695. (f) Colon, I.; Kelsey, R. D. *J. Org. Chem.* **1986**, *51*, 2627–2637. (g) Iyoda, M.; Otsuka, H.; Sato, K.; Nisato, N.; Oda, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80–87.

(3) (a) Clark, F. R.; Norman, R. O. C.; Thomas, C. B. *J. Chem. Soc., Perkin Trans I* **1975**, 121–125. (b) Jutand, A.; Mosleh, A. *Synlett* **1993**, 568–570. (c) Hassan, J.; Penalva, V.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Tetrahedron* **1998**, *54*, 13793–13804. (d) Penalva, V.; Hassan, J.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Tetrahedron Lett.* **1998**, *39*, 2559–2560. (e) Albanese, D.; Landini, D.; Penso, M.; Petricci, S. *Synlett* **1999**, 199–200. (f) Hennings, D. D.; Iwama, T.; Rawel, V. H. *Org. Lett.* **1999**, *1*, 1205–1208. (g) Kuroboshi, M.; Waki, Y.; Tanaka, H. *J. Org. Chem.* **2003**, *68*, 3938–3942. (h) Barluenga, J.; Moriel, P.; Aznar, F.; Valdés, C. *Org. Lett.* **2007**, *9*, 275–278.

(4) (a) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1469. (b) Nelson, T. D.; Crouch, R. D. *Org. React.* **2004**, *63*, 265–555.

(5) Yamamoto, T. *Macromol. Rapid Commun.* **2002**, *23*, 583–606.

(6) (a) de Meijere, A., Diederich, F., Eds. *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; Wiley-VCH, Weinheim, Germany, 2004. (b) Espinet, P.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4704–4734.

(7) For diene formation as a side reaction of cross-coupling, see: (a) Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Organomet. Chem.* **1987**, *334*, 181–194. (b) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813–817. (c) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393–2401. (d) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 4909–4914. (e) Rossi, R.; Carpita, A.; Cossi, P. *Tetrahedron* **1992**, *48*, 8801–8824. (f) Wang, Z.; Wnuk, S. F. *J. Org. Chem.* **2005**, *70*, 3281–3284. (g) Andrei, D.; Wnuk, S. F. *J. Org. Chem.* **2006**, *71*, 405–408. (h) Batsanov, A. S.; Knowles, J. P.; Whiting, A. *J. Org. Chem.* **2007**, *72*, 2525–2532.

(8) Osakada, K. In *Current Methods in Inorganic Chemistry*; Yamamoto, A., Kurosawa, H., Eds.; Elsevier: Amsterdam, 2003; Vol. 3, Chapter 5.

(9) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547–7560.

(10) (a) Yamamoto, T.; Wakabayashi, S.; Osakada, K. *J. Organomet. Chem.* **1992**, *428*, 223–237. (b) Yagyu, T.; Hamada, M.; Osakada, K.; Yamamoto, T. *Organometallics* **2001**, *20*, 1087–1101. (c) Suzaki, Y.; Osakada, K. *Organometallics* **2003**, *22*, 2193–2195. (d) Suzaki, Y.; Osakada, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 139–145. (e) Suzaki, Y.; Yagyu, T.; Osakada, K. *J. Organomet. Chem.* **2007**, *692*, 326–342.

(11) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627–2637.

(12) (a) Amatore, C.; Jutand, A. *Organometallics* **1988**, *7*, 2203–2214. (b) Jutand, A.; Mosleh, A. *J. Org. Chem.* **1997**, *62*, 261–274. (c) Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254–278. (d) Jutand, A. *Eur. J. Inorg. Chem.* **2003**, 2017–2040.

(13) (a) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174–4181. (b) Son, T.; Yanagihara, H.; Ozawa, F.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1251–1258.

(14) P–C reductive elimination giving alkenylphosphonium complexes has been reported: (a) Rybin, L. V.; Petrovskaya, E. A.; Rubinskaya, M. I.; Kuz'mina, L. G.; Struchkov, Y. T.; Kaverin, V. V.; Koneva, N. Y. *J. Organomet. Chem.* **1985**, *288*, 119–129. (b) Duan,

J.-P.; Liao, F.-L.; Wang, S.-L.; Cheng, C.-H. *Organometallics* **1997**, *16*, 3934–3940. (c) Huang, C.-C.; Duan, J.-P.; Wu, M.-Y.; Liao, F.-L.; Wang, S.-L.; Cheng, C.-H. *Organometallics* **1998**, *17*, 676–682.

(15) (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).

(16) (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.

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

(18) (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.

(19) 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.

(20) 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.

(21) (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.

(22) 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 $[Pd\{\eta^2\text{-}(E)\text{-}PhCH{=}CHPMePh_2\}(PMePh_2)_2]Br$ by the coordination of $PMePh_2$, the formation of **A** is possibly hindered by increasing coordination stability of the styrylphosphonium ligand.

(23) (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.

(24) Dolby, L. J.; Wilkins, C.; Frey, T. G. *J. Org. Chem.* **1966**, *31*, 1110–1116.

(25) Kim, S. H.; Wei, H.-X.; Willis, S.; Li, G. *Synth. Commun.* **1999**, *29*, 4179–4185.

(26) Coulson, D. R. *Inorg. Synth.* **1971**, *13*, 121–124.

(27) Louch, W. J.; Eaton, D. R. *Inorg. Chim. Acta* **1978**, *30*, 243–250.

(28) Hartley, F. R. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 119–137.

(29) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220–223.

(30) Kuran, W.; Musco, A. *Inorg. Chim. Acta* **1975**, *12*, 187–193.

(31) Ukai, T.; Kawamura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, 65, 253–266.

Chapter 4

Mechanism of P–C Reductive Elimination from *trans*-[Pd(CH=CHPh)Br($PMePh_2$)$_2$]

Abstract

The (*E*)- and (*Z*)-styryl isomers of *trans*-[Pd(CH=CHPh)Br($PMePh_2$)$_2$] (**1a**) and [Pd(η^2-PhCH=CHP$MePh_2$)Br($PMePh_2$)] (**2a**) were prepared, and their P–C reductive elimination (**1a** → **2a**) and P–C oxidative addition (**2a** → **1a**) behaviors were examined. Kinetics and thermodynamics of the reactions are strongly affected by E/Z configurations of styryl group and solvent polarity. Complex (*E*)-**1a** readily undergoes P–C reductive elimination in CD_2Cl_2 as a polar solvent in high selectivity. On the other hand, while the (*Z*)-isomer of **1a** is unreactive toward reductive elimination, (*Z*)-**2a** undergoes P–C oxidative addition favorably in non-polar benzene. X-ray diffraction analysis and DFT calculations for **1a** and **2a** provided reasonable accounts for these reaction features. Kinetic examinations revealed two types of P–C reductive elimination processes, which involve pre-dissociation and association of $PMePh_2$ ligand, respectively.

Introduction

Reductive elimination is a crucial elementary process, often serving as the product-forming step in many catalytic organic transformations.[1] Besides classical reactions to afford C–H and C–C bonds, reductive elimination of a carbon–heteroatom bond has attracted considerable recent attention in connection with palladium-catalyzed synthesis of heteroatom compounds.[2] While the C–N and C–O bond formations are of central importance in such chemistry, there has been a growing interest in P–C reductive elimination of hydrocarbyl and phosphine ligands from Pd(II) complexes.[3–7] It has been documented that complexes of the formula $[PdAr(X)(PAr'_3)_2]$ (Ar, Ar' = aryl; X = halogen) undergo P–C reductive elimination to give arylphosphonium halides ($[PArAr'_3]^+X^-$) and Pd(0) species.[3] This reaction is usually reversible with P–C oxidative addition, and the overall process results in Ar/Ar' exchange between palladium and phosphorus atoms.[8] The P–C reductive elimination has also been postulated for catalytic formation of aryl-,[4] alkenyl-,[5] and alkyl-phosphoniums,[6] and functionalized phosphines.[7]

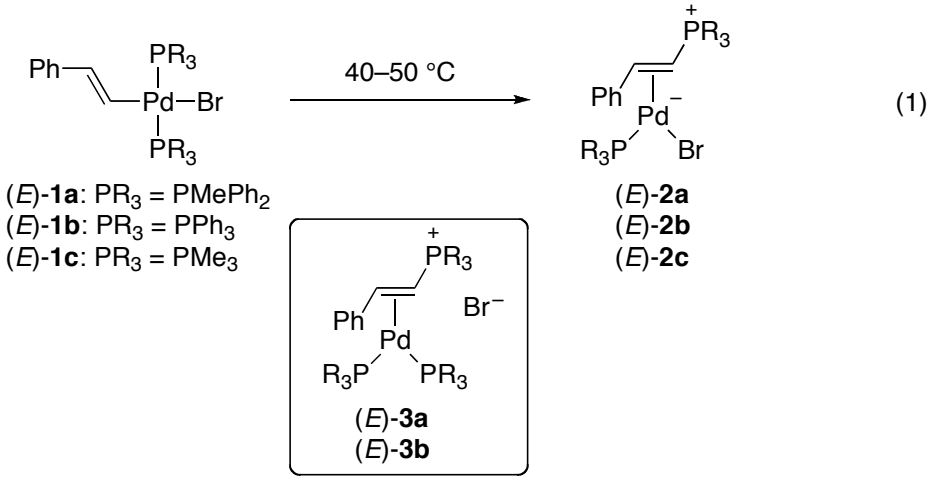
Most of the reductive elimination processes involve the coupling of two anionic ligands. In contrast, P–C reductive elimination causes the bond-formation between anionic and neutral ligands. Accordingly, it is expected that the reaction possesses rather unique mechanistic features, differing significantly from common reductive elimination processes. Although the reductive elimination of arylphosphonium from $[PdAr(X)(PAr'_3)_2]$ type complexes has been suggested to involve prior dissociation of one of the phosphine ligand,[3a–c] intimate information about the mechanism of P–C reductive elimination is still limited.[9] This is probably due to the concurrent operation of P–C oxidative addition, which makes the reaction system complicated.

As shown in Chapter 3, the homo-coupling reaction of (*E*)-styryl bromide promoted by a palladium(0) phosphine complex is induced by P–C reductive elimination from $[Pd(CH{=}CHPh)(Br)(PAr'_3)_2]$ as a catalytic intermediate. This chapter deals with the mechanism of P–C reductive elimination from *trans*-$[Pd(CH{=}CHPh)Br(PMePh_2)_2]$ (**1a**) to

give [Pd(η^2-PhCH=CHPMePh$_2$)Br(PMePh$_2$)] (**2a**) and [Pd(η^2-PhCH=CHPMePh$_2$)-(PMePh$_2$)$_2$]Br (**3a**). Unlike the reactions of arylpalladium complexes,[3] the P–C reductive elimination of styryl complexes forms η^2-styrylphosphonium complexes as the products, which are sufficiently stable for isolation.[10] Therefore, the reaction has been successfully investigated in detail by kinetic experiments. The author herein describes that P–C reductive elimination of **1a** is strongly dependent on E/Z configurations of styryl ligand. It will be also shown that two types of reductive elimination processes are operative, depending on the amount of free PMePh$_2$ in the system.

Results and Discussion

P–C Reductive Elimination and Oxidative Addition Reactions. (*E*)-styryl complexes having three kinds of tertiary phosphine ligands ((*E*)-**1a**–**c**) were heated in solution, and the reaction systems were examined at intervals by ^{1}H NMR spectroscopy (eq 1). The results are summarized in Table 1.



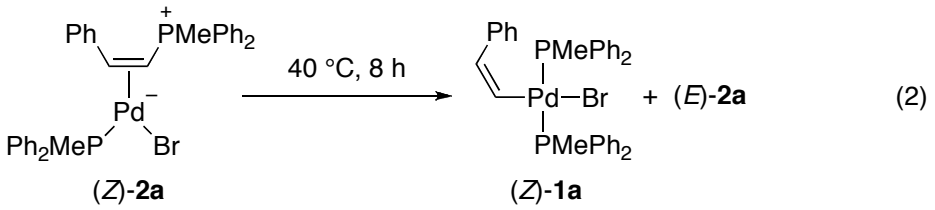
Complex (*E*)-**1a** bearing $PMePh_2$ ligands readily underwent P–C reductive elimination in CD_2Cl_2 at 40 °C to give the corresponding styrylphosphonium complex ((*E*)-**2a**) in 82% selectivity (run 1). The remaining part of (*E*)-**1a** was converted to *trans*-$[PdBr_2(PMePh_2)_2]$ (5%) and some unidentified palladium species. The author already confirmed that the dibromo complex is afforded by disproportionation of (*E*)-**1a**, and its formation is inhibited by free $PMePh_2$.[11] Actually, in the presence of added $PMePh_2$ (1 equiv/**1a**), the P–C reductive elimination proceeded in 97% selectivity (run 2), where the product styrylphosphonium complex was obtained as $[Pd\{\eta^2\text{-}(E)\text{-}PhCH{=}CHPMePh_2\}(PMePh_2)_2]Br$ ((*E*)-**3a**), instead of (*E*)-**2a**.[12] The conversion of (*E*)-**1a** was strongly affected by solvent polarity; the reaction decelerated significantly in THF and benzene, and the selectivity of (*E*)-**2a** decreased (runs 3 and 4). The PPh_3 complex (*E*)-**1b** behaved similarly, while the reactivity was apparently higher than that of (*E*)-**1a** (runs 5 and 6). On the other hand, the PMe_3 complex (*E*)-**1c** was much less reactive than (*E*)-**1a** and (*E*)-**1b** (run 7).

Table 1. P–C Reductive Elimination of *trans*-[Pd{CH=CHPh-(*E*)}Br(PR_3)$_2$] ((*E*)-**1**)[a]

run	complex	solvent	additive (PR_3, mM)	temp (°C)	$t_{1/2}$[b] (min)	selectivity of **2** (or **3**) (%)
1	(*E*)-**1a**	CD_2Cl_2	0	40	ca. 5	82
2	(*E*)-**1a**	CD_2Cl_2	50	40	168	97[c]
3	(*E*)-**1a**	THF-d_8	0	50	48	67
4	(*E*)-**1a**	C_6D_6	0	50	60	56
5	(*E*)-**1b**	CD_2Cl_2	0	40	<4	63
6	(*E*)-**1b**	CD_2Cl_2	50	40	35	96[d]
7	(*E*)-**1c**	CD_2Cl_2	0	40	270	43[e]

[a] [**1**]$_0$ = 50 mM. All reactions were examined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [b] Half-lives of **1**. [c] The sum of [Pd{η^2-(*E*)-PhCH=CHPMePh$_2$}(PMePh$_2$)$_2$]Br ((*E*)-**3a**) (96%) and (*E*)-[PhCH=CH-PMePh$_2$]$^+$Br$^-$ (1%). [d] The product was [Pd{η^2-(*E*)-PhCH=CHPPh$_3$}(PPh$_3$)$_2$]Br ((*E*)-**3b**). [e] The selectivity at 58% conversion of (*E*)-**1c**.

Unlike the (*E*)-styryl complexes, the (*Z*)-isomer *trans*-[Pd{CH=CHPh-(*Z*)}-Br(PMePh$_2$)$_2$] ((*Z*)-**1a**) was stable toward P–C reductive elimination; no trace of [Pd{η^2-(*Z*)-PhCH=CHPMePh$_2$}Br(PMePh$_2$)] ((*Z*)-**2a**) was formed at 50 °C for 6 h. On the contrary, (*Z*)-**2a** was found to undergo oxidative addition of styrylphosphonium ligand (eq 2, Table 2). Heating a C_6D_6 solution of isolated (*Z*)-**2a** at 40 °C for 8 h resulted in the formation of (*Z*)-**1a** in 46% selectivity, together with (*E*)-**2a** (33%) and other palladium complexes including *trans*-[PdBr$_2$(PMePh$_2$)$_2$] (4%) (run 1). The formation of (*Z*)-**1a** was entirely suppressed by added PMePh$_2$ (1 equiv/**1a**), while the Z-to-E isomerization of styrylphosphonium ligand giving (*E*)-**2a** continued to proceed at a comparable rate (run 2). The reaction rate and the selectivity of (*Z*)-**1a** decreased significantly in CD_2Cl_2 as a polar solvent (run 3).



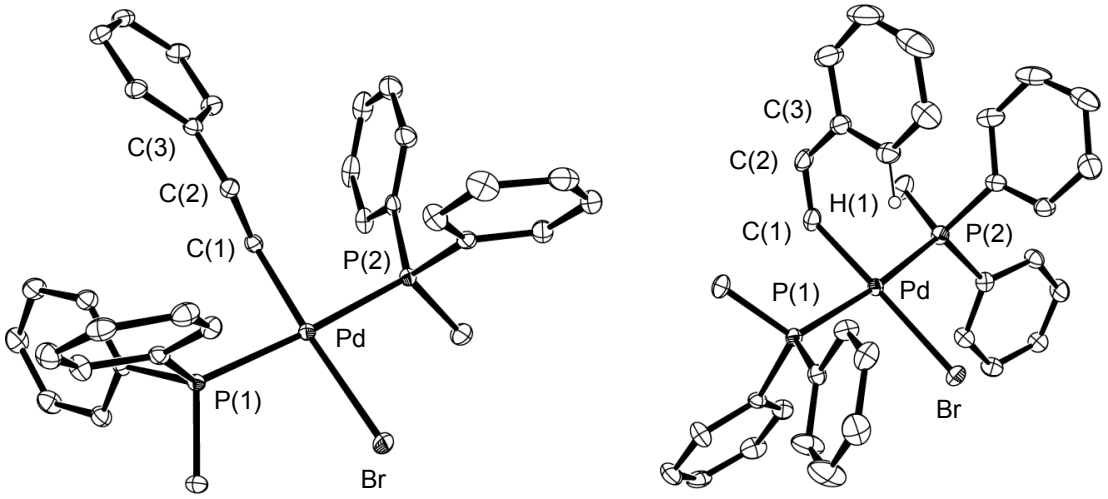
(2)

Table 2. P–C Oxidative Addition of [Pd{η^2-(*Z*)-PhCH=CHPMePh$_2$}Br(PMePh$_2$)] ((*Z*)-**2a**)[a]

run	solvent	$PMePh_2$ (mM)	conversion of (*Z*)-**2a** (%)	selectivity (%)	
				(*Z*)-**1a**	(*E*)-**2a**
1	C_6D_6	0	79	46	33
2	C_6D_6	10	90	0	100
3	CD_2Cl_2	0	27	12	73

[a] $[(Z)\text{-}\mathbf{2a}]_0$ = 10 mM. All reactions were run at 40 °C for 8 h.

X-Ray Structures of 1a and 2a. It has been found that reductive elimination and oxidative addition reactions of P–C bonds are markedly affected by E/Z configurations of styryl group and solvent polarity. Since these reactions are essentially reverse processes, and the conversion of (*E*)-**1a** to (*E*)-**2a** and that of (*Z*)-**2a** to (*Z*)-**1a** are operative under similar conditions, it seems likely that the observed tendencies mainly reflect the difference in thermodynamic stability between (*E*)- and (*Z*)-isomers of **1a** and **2a**. The author therefore examined their structures by X-ray diffraction analysis and DFT calculations.



(*E*)-**1a** (*Z*)-**1a**

Figure 1. X-ray structures of (*E*)-**1a** and (*Z*)-**1a** (one of the crystallographically independent molecules). The thermal ellipsoids are drawn at the 30% probability levels. Hydrogen atoms, expect for the H(1) atom of (*Z*)-**1a**, are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows. (*E*)-**1a**: Pd–Br = 2.5324(8), Pd–P(1) = 2.3139(10), Pd–P(2) = 2.3121(10), Pd–C(1) = 2.007(2), C(1)–C(2) = 1.325(3), Br–Pd–P(1) = 94.15(2), Br–Pd–P(2) = 90.08(3), C(1)–Pd–P(1) = 88.32(7), C(1)–Pd–P(2) = 87.50(7), Pd–C(1)–C(2) = 128.85(18), C(1)–C(2)–C(3) = 123.4(2). (*Z*)-**1a**: Pd–Br = 2.5233(8), Pd–P(1) = 2.3187(12), Pd–P(2) = 2.3128(13), Pd–C(1) = 2.002(5), C(1)–C(2) = 1.341(7), Br–Pd–P(1) = 91.50(3), Br–Pd–P(2) = 95.55(3), C(1)–Pd–P(1) = 87.21(13), C(1)–Pd–P(2) = 85.75(13), Pd–C(1)–C(2) = 129.5(4), C(1)–C(2)–C(3) = 129.4(4).

Figure 1 shows ORTEP drawings of (*E*)-**1a** and (*Z*)-**1a**. Both complexes have similar structures with comparable distances of Pd–C (2.00 Å), Pd–P (2.31 Å), and Pd–Br (2.53 Å) bonds. A notable difference between the isomers is found for the orientation of styryl ligands. The (*E*)-styryl ligand in (*E*)-**1a** is oriented away from the palladium center, successfully evading the steric congestion within the molecule. On the other hand, the phenyl group of the (*Z*)-styryl ligand in (*Z*)-**1a** is situated over the palladium center. Although the interatomic distance of Pd···H(1) (2.494 Å) is in a range of agostic interaction, it seems likely to consider a repulsive interaction between them, because the C(1)–C(2)–C(3) angle (129.4(4)°) is significantly enlarged as compared with that of (*E*)-**1a** (123.4(2)°).

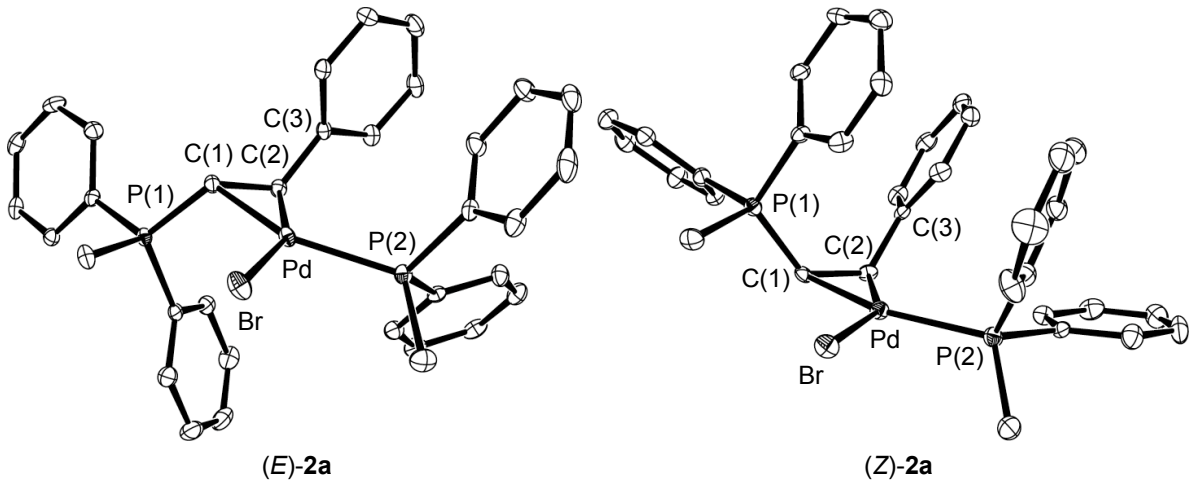


Figure 2. X-ray structures of (*E*)-**2a** and (*Z*)-**2a**. The thermal ellipsoids are drawn at the 30% probability levels. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows. (*E*)-**2a**: Pd–Br = 2.5669(10), Pd–P(2) = 2.281(2), Pd–C(1) = 2.135(8), Pd–C(2) = 2.063(7), C(1)–P(1) = 1.758(8), C(1)–C(2) = 1.444(10), C(2)–C(3) = 1.491(10), Br–Pd–P(2) = 98.32(6), C(1)–Pd–C(2) = 40.2(3), Pd–C(1)–C(2) = 67.2(4), C(1)–Pd–Br = 115.1(2), C(2)–Pd–P(2) = 106.4(2), C(1)–C(2)–C(3) = 122.0(7), P(1)–C(1)–C(2) = 122.2(6). (*Z*)-**2a**: Pd–Br = 2.6201(10), Pd–P(2) = 2.2872(17), Pd–C(1) = 2.106(5), Pd–C(2) = 2.088(5), C(1)–P(1) = 1.754(5), C(1)–C(2) = 1.438(7), C(2)–C(3) = 1.494(7), Br–Pd–P(2) = 92.78(4), C(1)–Pd–C(2) = 40.1(2), Pd–C(1)–C(2) = 69.3(3), C(1)–Pd–Br = 111.83(15), C(2)–Pd–P(2) = 115.24(16), C(1)–C(2)–C(3) = 124.8(4), P(1)–C(1)–C(2) = 129.6(4).

Figure 2 shows the X-ray structures of (*E*)-**2a** and (*Z*)-**2a**. The C(1)–C(2) distances (1.444(10), 1.438(7) Å) are comparable to each other. The Pd, C(1), C(2), P(2), and Br atoms are coplanar in both molecules as previously observed for related alkenylphosphonium complexes.[5a,b] The Pd–C(1) bonds (2.135(8), 2.106(5) Å) are apparently longer than the Pd–C(2) bonds (2.063(7), 2.088(5) Å), reflecting the higher trans-influence of $PMePh_2$ than Br.

A remarkable structural feature of (*Z*)-**2a** is the axial/axial/axial arrangement of three phenyl groups of $PhCH{=}CHP^{(1)}MePh_2$ and $P^{(2)}MePh_2$ ligands. Since they are situated at 1,3-diaxial positions with one another, a great deal of steric repulsion should take place

between them. This situation makes a sharp contrast with (*E*)-**2a**, in which all substituents are accommodated with enough space. Actually, the P(1)–C(1)–C(2) angle of (*Z*)-**2a** (129.6(4)°) is apparently wider than that of (*E*)-**2a** (122.2(6)°).

DFT Calculations. Table 3 lists the relative energies of **2a** to **1a**, estimated by DFT calculations. The geometry optimization of (*E*)- and (*Z*)-isomers of the complexes was carried out using B3LYP in conjunction with the LANL2DZ basis set and effective core potential for Pd and 6-31G(d) basis set for other atoms, where diffuse function was added for Br atom. Solvent effects were incorporated by PCM single-point calculations on fully optimized geometries in vacuo. The optimized structures were in well accordance with the X-ray structures given in Figures 1 and 2.

The data in Table 3 clearly indicate that P–C reductive elimination of (*E*)-isomer [(*E*)-**1a** → (*E*)-**2a**] is an exothermic process, whereas that of (*Z*)-isomer [(*Z*)-**1a** → (*Z*)-**2a**] is endothermic (i.e., the reverse process is exothermic). It is also seen that **2a** is more effectively stabilized than **1a** in polar solvents, irrespective of the E/Z configurations of styryl group. These tendencies are consistent with the experimental observations described above.

Table 3. Relative Energies of **2a** to **1a** (kcal mol^{-1}) [a]

solvent	(*E*)-isomers	(*Z*)-isomers
(in vacuo)	0.0	+4.3
C_6H_6	–2.3	+2.3
THF	–4.2	+0.4
CH_2Cl_2	–4.6	+1.0

[a] The values of $E_{\mathbf{2a}} - E_{\mathbf{1a}}$, estimated by DFT calculations.

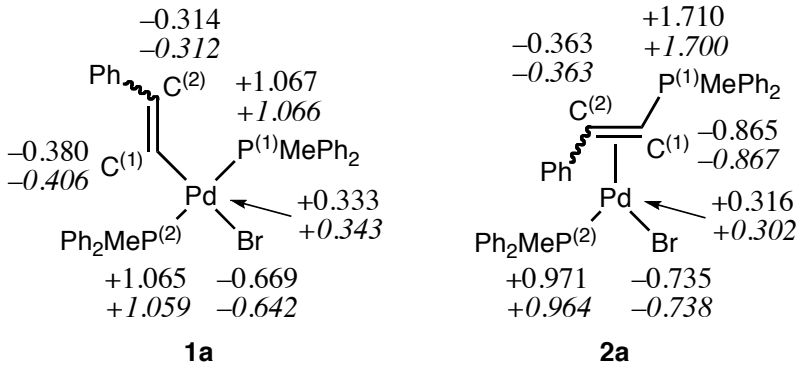


Figure 3. NBO charges on the core atoms of **1a** and **2a**. The values for (*E*)- and (*Z*)-isomers are given with roman and italic typefaces, respectively.

Figure 3 compares charge distribution in **1a** and **2a**, evaluated by NBO analysis. The values written in roman and italic letters correspond to the atomic charges for (*E*)- and (*Z*)-isomers, respectively. The η^2-styrylphosphonium palladium complexes (**2**) are commonly depicted as zwitter ionic species having positive and negative charges on the phosphorus and palladium atoms, respectively (see eqs 1 and 2). However, while the P(1) atom of **2a** is charged positively, the Pd atom is not charged negatively in reality. The negative charge is distributed on the C(1), C(2) and Br atoms, and most remarkably increased on the C(1) atom as compared with **1a**, showing the occurrence of strong π-back donation from the palladium center to the η^2-styrylphosphonium ligand in **2a**.

Mechanism of P–C Reductive Elimination. As seen from Table 1 (runs 1, 2), the P–C reductive elimination of (*E*)-**1a** is strongly inhibited by added $PMePh_2$, showing a reaction process involving pre-dissociation of $PMePh_2$ ligand (path (a) in Scheme 1). The three-coordinate intermediate **A** undergoes P–C reductive elimination to form **B**, which combines with $PMePh_2$ to afford (*E*)-**2a**. On the other hand, as described below, kinetic data revealed that the other reaction process involving prior association of $PMePh_2$ is operative in the presence of added $PMePh_2$ (path (b)).

Scheme 1. Proposed Mechanisms for P–C Reductive Elimination of (*E*)-**1a**

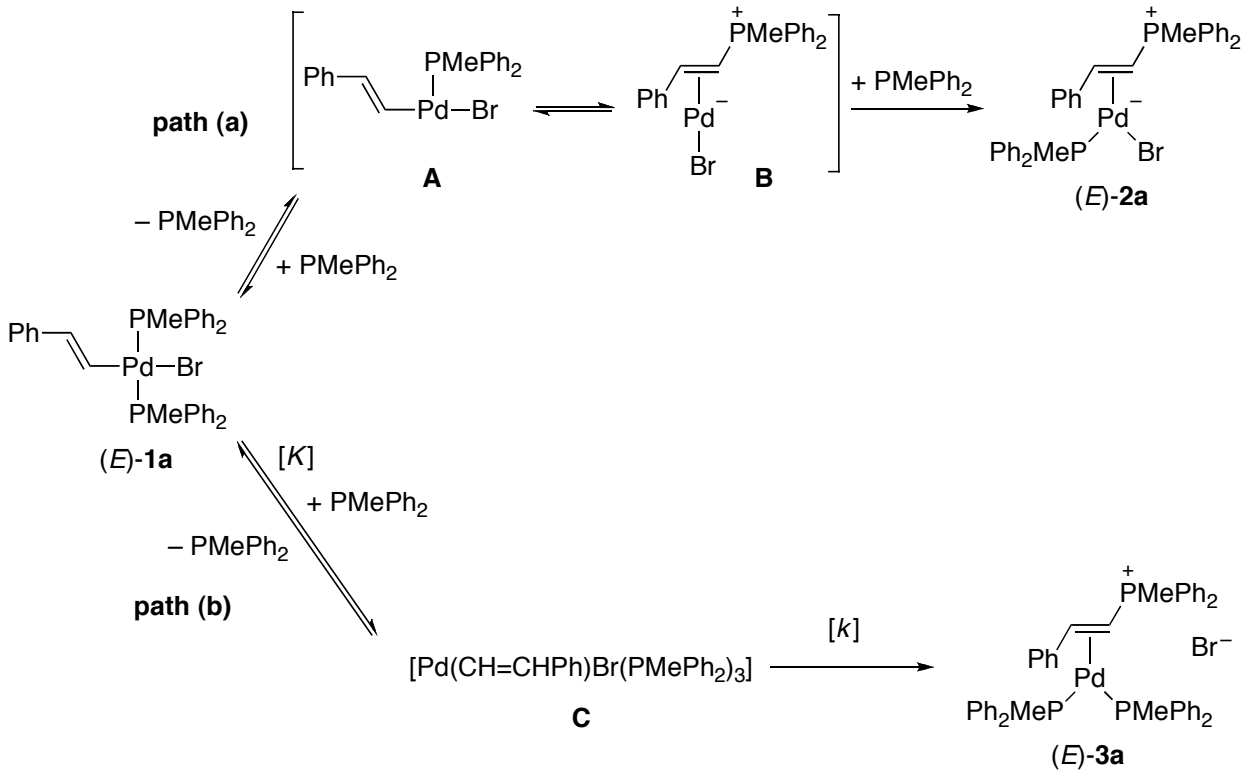


Figure 4 shows the time-course of conversion of (*E*)-**1a** (50 mM) in CD_2Cl_2 at 40 °C, followed by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. In the absence of free $PMePh_2$ (run 1), the PMe signal of (*E*)-**1a** at δ 2.07 rapidly decreased ($t_{1/2}$ = ca. 5 min) to be replaced by the PMe signals of (*E*)-**2a** at δ 2.83 and 1.50. The reaction progress was effectively prevented by addition of a small amount of $PMePh_2$ (5 mM, 0.1 equiv/**1a**) to the system (run 2). In this case, however, the reaction dramatically accelerated from the middle stage, because the added $PMePh_2$ is consumed by trapping in the reductive elimination product as [Pd{η^2-(*E*)-PhCH=CHPMePh_2}($PMePh_2$)$_2$]Br ((*E*)-**3a**). Indeed, in the ^{1}H NMR spectra, the PMe signal of (*E*)-**1a** was observed coalescent with that of $PMePh_2$ until ca. 20% conversion of (*E*)-**1a**, but thereafter changed to a sharp triplet, showing the absence of free $PMePh_2$ in the system.

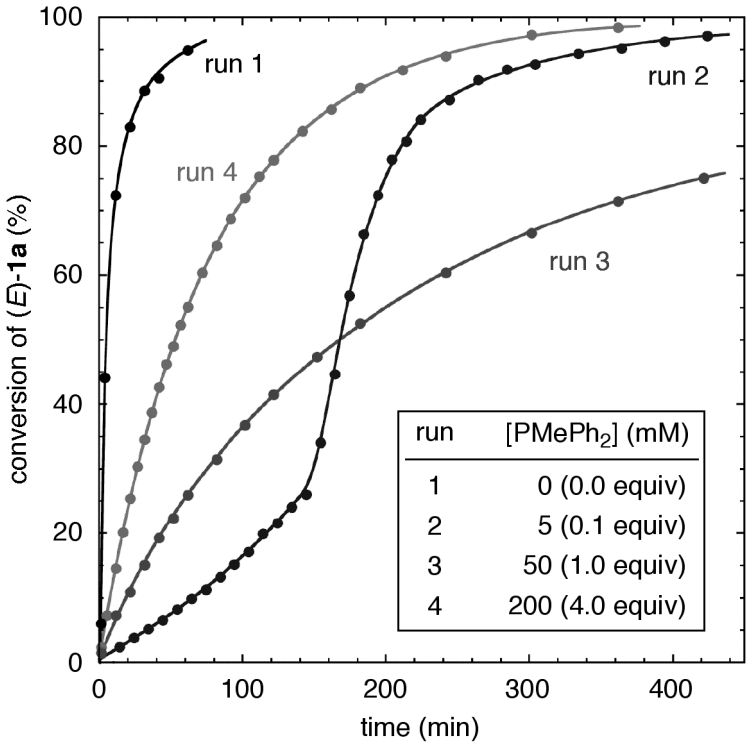


Figure 4. The time-course of conversion of (*E*)-**1a** (50 mM) in CD_2Cl_2 at 40 °C in the absence or presence of added $PMePh_2$.

Interestingly, the rate of P–C reductive elimination increased significantly with increasing amounts of added $PMePh_2$ (runs 3 and 4). Thus, the reaction performed with 50 mM of $PMePh_2$ (run 3) was clearly faster than the initial stage of run 2 (5 mM), and accelerated further with 200 mM of $PMePh_2$ (run 4). Although the concentration of free $PMePh_2$ gradually decreases with the formation of (*E*)-**3a**, the reactions obeyed a good first-order kinetics ($r > 0.999$) up to 19 (run 3) and 60% (run 4) conversion of (*E*)-**1a**. Table 4 lists the rate-constants (k_{obsd}) thus estimated. The plot of $1/k_{obsd}$ against $1/[PMePh_2]$ exhibited a good linear correlation ($r = 0.995$, Figure 5).

These kinetic observations are consistent with the reaction process of path (b) in Scheme 1. Since (*E*)-**1a** undergoes rapid ligand-exchange with free $PMePh_2$ in an NMR time-scale, it is likely to assume the occurrence of rapid equilibrium between (*E*)-**1a** and **C**. Intermediate **C** then undergoes the rate-determining formation of (*E*)-**3a**. In this case, the

reaction rate can be expressed by eq 3, where [Pd-styryl] = [(*E*)-**1a**] + [**C**], K = [**C**]/[(*E*)-**1a**][$PMePh_2$], and k stands for the rate-constant for the conversion of **C** to (*E*)-**3a**:

$$\frac{d[(E)\text{-}\mathbf{3a}]}{dt} = -\frac{d[\text{Pd-styryl}]}{dt} = \frac{kK[PMePh_2]}{1 + K[PMePh_2]}[\text{Pd-styryl}] \qquad (3)$$

Consequently, the k_{obsd} values are correlated with the [$PMePh_2$] values by the following equation:

$$\frac{1}{k_{obsd}} = \frac{1}{kK[PMePh_2]} + \frac{1}{k} \qquad (4)$$

Applying the slope and intercept values of Figure 5 to eq 4 results in the following rate and equilibrium constants: $k = 4.8 \times 10^{-4}$ s^{-1}, $K = 3.7$ M^{-1}.

Table 4. Effects of Added $PMePh_2$ on the First-order Rate Constants for P–C Reductive Elimination of (*E*)-**1a** [a]

[$PMePh_2$] (mM)	$10^4 k_{obsd}$ (s^{-1})	data range (%) [b]
50	0.76(2)	19
64	0.87(1)	29
100	1.28(2)	38
200	2.14(1)	60

[a] [(*E*)-**1a**]$_0$ = 50 mM. All reactions were run at 40 °C in CD_2Cl_2. [b] The upper range of the conversion of (*E*)-**1a**, taken into the first-order plot.

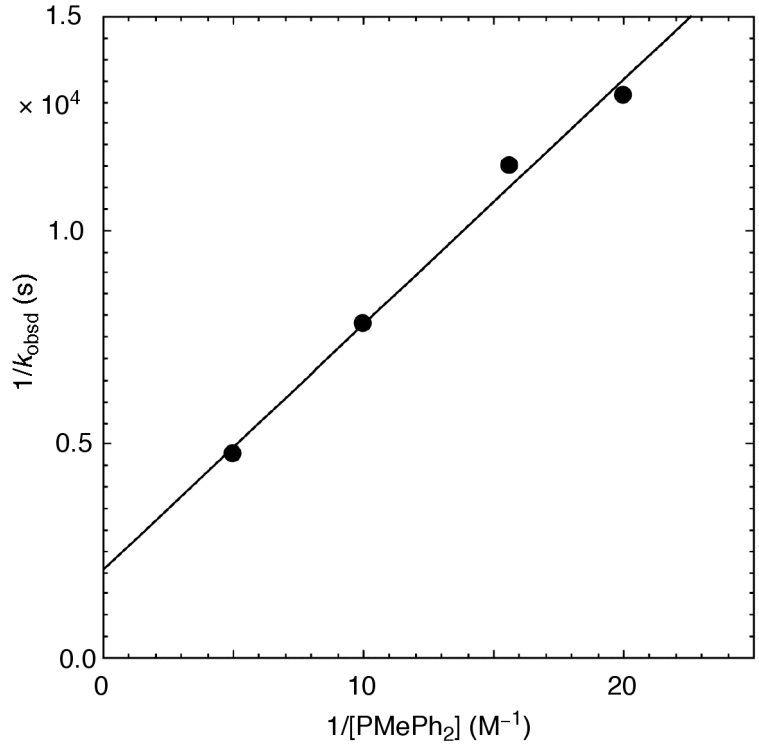
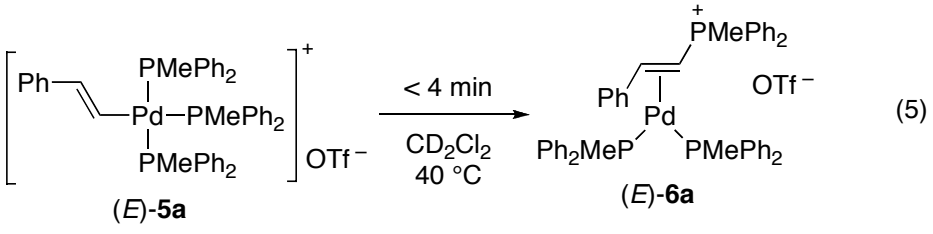


Figure 5. Plot of $1/k_{obsd}$ against $1/[PMePh_2]$ for the kinetic data in Table 4. The straight line is based on least-squares calculation: $1/k_{obsd} = (5.7(4) \times 10^2 \text{ s M})/[PMePh_2] + (2.1(5) \times 10^3 \text{ s})$.

There are two possible structures for intermediate **C**. One is a five-coordinate species, whereas the other is a four-coordinate ionic complex $[Pd\{CH{=}CHPh\text{-}(E)\}(PMePh_2)_3]^+Br^-$ ((*E*)-**4a**), generated by ligand displacement of Br in (*E*)-**1a** with $PMePh_2$. The P–C reductive elimination from the latter type intermediate has been postulated for catalytic conversion of alkenyl triflates and PPh_3 to alkenylphosphonium triflates.[5c,d] The author therefore prepared $[Pd\{CH{=}CHPh\text{-}(E)\}(PMePh_2)_3]^+OTf^-$ ((*E*)-**5a**) as a model of (*E*)-**4a**, and examined its reactivity toward P–C reductive elimination (eq 5).



(5)

Treatment of (*E*)-**1a** (50 mM) with AgOTf (1 equiv) in CD_2Cl_2 in the presence of $PMePh_2$ (1 equiv) at –30 °C for 1 h formed (*E*)-**5a** in 96% selectivity. The resulting (*E*)-**5a** was highly reactive toward P–C reductive elimination; the reaction was completed within a few minutes at 40 °C to give [Pd{η^2-(*E*)-PhCH=CHP$MePh_2$}$(PMePh_2)_2$]OTf ((*E*)-**6a**) in 95% selectivity. No notable change in the reaction rate was observed in the presence of excess $PMePh_2$ (4 equiv). Since the observed reactivity of (*E*)-**5a** ($k > 5 \times 10^{-3}$ s^{-1} at 40 °C) is at least 10 times higher than that of **C** ($k = 4.8 \times 10^{-4}$ s^{-1}), it is convincing that **C** is not the ionic species like (*E*)-**5a**, but either a five-coordinate species or a tight ion pair of [Pd{CH=CHPh-(*E*)}$(PMePh_2)_3$]$^+$ and Br^-. Complex **C** is then converted to (*E*)-**3a** by either a stepwise mechanism involving a metallophosphorane intermediate [Pd{P(CH=CHPh)-$MePh_2$}$Br(PMePh_2)_2$][13] or a concerted mechanism with concurrent formation of the P–CH=CH and Pd–(η^2-CH=CH) bonds.

Conclusions

It has been evidenced that P–C reductive elimination of *trans*-[Pd{(CH=CHPh)-$Br(PMePh_2)_2$} (**1a**) is essentially a reverse process with P–C oxidative addition of styrylphosphonium complex [Pd{η^2-PhCH=CHP$MePh_2$}$Br(PMePh_2)$] (**2a**). The inter-conversion between **1a** and **2a** is markedly dependent on E/Z configurations of styryl group and solvent polarity. The (*E*)-isomer of **1a** undergoes P–C reductive elimination easily in polar CD_2Cl_2 to afford (*E*)-**2a** in high selectivity, whereas P–C oxidative addition of (*Z*)-**2a** giving (*Z*)-**1a** takes place favorably in non-polar C_6D_6. These tendencies have been rationalized by X-ray structural analysis and DFT calculations for **1a** and **2a**. Complex **2a** bearing styrylphosphonium ligand is a significantly charged molecule, compared with **1a**, to cause a strong solvent effect. Moreover, complex (*Z*)-**2a** is sterically unstable due to the occurrence of 1,3-diaxial interactions of phenyl groups within the molecule, and thereby converted to (*Z*)-**1a** by P–C oxidative addition.

The reductive elimination from [PdR(R')L_2] type complexes has been known to proceed via any of three reaction processes: (a) dissociative path via a three-coordinate intermediate, (b) direct path, and (c) associative path with pre-coordination of an external L to give a [PdR(R')L_3] intermediate.[1a] The reaction processes vary with hydrocarbyl ligands, and alkenyl complexes generally follow the direct path (b).[14] On the other hand, the present P–C reductive elimination from (*E*)-**1a** has been found to proceed via either dissociative path (a) or associative path (c), depending on the amount of free $PMePh_2$ in the system. In the absence of free $PMePh_2$, the reaction invokes pre-dissociation of one of the $PMePh_2$ ligands, giving a three-coordinate [Pd(CH=CHPh)Br($PMePh_2$)] intermediate, which undergoes P–C reductive elimination. This process is effectively suppressed by addition of $PMePh_2$ to the system, and an alternative process involving prior association of (*E*)-**1a** with $PMePh_2$ takes place. Comparison of the kinetic data with that of [Pd{CH=CHPh-(*E*)}$(PMePh_2)_3$]$^+$OTf$^-$ ((*E*)-**5a**) has suggested the intermediacy of a five-coordinate species or a tight ion pair of [Pd{CH=CHPh-(*E*)}$(PMePh_2)_3$]$^+$ and Br^-, rather than the four-coordinate ionic species like (*E*)-**5a**.

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk techniques. Nitrogen and argon gases 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. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University. CD_2Cl_2, THF-d_8, and C_6D_6 were dried over CaH_2, Na/Ph_2CO, and $LiAlH_4$, respectively, distilled, and stored over activated MS4A. The compounds *trans*-[Pd{CH=CHPh-(*E*)}-

$Br(PMePh_2)_2]$ ((*E*)-**1a**),[11] *trans*-[Pd{CH=CHPh-(*Z*)}$Br(PMePh_2)_2$] ((*Z*)-**1a**),[14a] [Pd{η^2-(*E*)-Ph-CH=CHP$MePh_2$}$Br(PMePh_2)$] ((*E*)-**2a**),[11] [Pd(η^5-C_5H_5)(η^3-C_3H_5)],[15] (*E*)-styryl bromide,[16] (*Z*)-P(CH=CHPh)Ph_2,[17] and [$Pd(dba)_2$][18] were prepared according to literatures. Other chemicals were purchased and used as received.

Synthesis of *trans*-[Pd{CH=CHPh-(*E*)}$Br(PPh_3)_2$] ((*E*)-1b). To a heterogeneous solution of [Pd(η^5-C_5H_5)(η^3-C_3H_5)] (106 mg, 0.500 mmol) and PPh_3 (275 mg, 1.05 mmol) in toluene (10 mL) was added (*E*)-styryl bromide (1.83 g, 10.0 mmol) at 0 °C. The mixture was stirred at room temperature until being homogeneous, and then was allowed to stand at the same temperature, causing precipitation of pale yellow crystals of (*E*)-**1b**, which was collected by filtration, washed successively with Et_2O, and dried under vacuum (385 mg, 95% yield). The NMR data was identical to those reported.[12] ^{1}H NMR (CD_2Cl_2): δ 7.70–7.63 and 7.43–7.30 (m, 30H in total), 6.98–6.87 (m, 3H), 6.40 (dt, $^3J_{HH}$ = 15.7 Hz, $^3J_{HP}$ = 9.7 Hz, 1H), 6.27 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 5.42 (dt, $^3J_{HH}$ = 15.8 Hz, $^4J_{HP}$ = 2.5 Hz, 1H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 24.5 (s).

Synthesis of *trans*-[Pd{CH=CHPh-(*E*)}$Br(PMe_3)_2$] ((*E*)-1c). To a homogeneous solution of [(η^5-C_5H_5)(η^3-C_3H_5)Pd] (106 mg, 0.500 mmol) in toluene (2.0 mL) was added PMe_3 (78.9 mg, 1.05 mmol) at 0 °C. The mixture was stirred for 10 min, and (*E*)-styryl bromide (366 mg, 2.00 mmol) was added. The solution was stirred at room temperature for 4 h. Hexane (5 mL) was added with stirring at 0 °C. A 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 dissolved in a minimum amount of CH_2Cl_2 (ca. 1 mL) at room temperature, layered with Et_2O (ca. 5 mL), and allowed to stand at the same temperature to afford pale yellow crystals of the title compound (165 mg, 74% yield). Mp: 118–120 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.33–7.21 and 7.12–7.07 (m, 6H in total), 6.43 (d, $^3J_{HH}$ = 16.5 Hz, 1H), 1.38 (virtual triplet, J = 3.5 Hz, 18H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 145.6 (t, $^3J_{PC}$ = 9 Hz), 140.4 (s), 134.3 (t, $^4J_{PC}$ = 6 Hz), 129.0 (s), 125.9 (s), 125.2 (s), 14.6 (t,

$^{1}J_{PC}$ = 15 Hz). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ –17.9 (s). Anal. Calcd for $C_{14}H_{25}BrP_2Pd$: C, 38.08; H, 5.71. Found: C, 37.96; H, 5.68.

Synthesis of [Pd{(*Z*)-η^2-PhCH=CHPMePh$_2$}Br(PMePh$_2$)] ((*Z*)-2a). (a) Synthesis of (*Z*)-[PhCH=CHPMePh$_2$]$^+$Br$^-$. A mixture of (*Z*)-P(CH=CHPh)Ph$_2$ (1.22 g, 4.25 mmol) and 2 M solution of MeBr in THF (22 mL, 44 mmol) was stirred at room temperature. After 48 h, a white precipitate generated from the solution was collected by filtration, washed successively with Et_2O, and dried under vacuum. Recrystallization of the crude product from a mixture of acetone and Et_2O at –20 °C gave pale yellow crystals of the title compound (1.33 g, 82% yield). Mp: 130 °C. ^{1}H NMR ($CDCl_3$): δ 8.30 (dd, $^{2}J_{HP}$ = 45.4 Hz, $^{3}J_{HH}$ = 13.2 Hz, 1H), 7.86–7.78, 7.73–7.67 and 7.63–7.57 (m, 10H in total), 7.22 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H), 7.13–7.05 (m, 3H), 7.01 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H), 2.74 (d, $^{3}J_{HP}$ = 13.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 158.0 (d, $^{4}J_{PC}$ = 1 Hz), 134.6 (d, $^{2}J_{PC}$ = 3 Hz), 133.5 (d, $^{3}J_{PC}$ = 8 Hz), 132.6 (d, $^{3}J_{PC}$ = 11 Hz), 130.4 (s), 130.3 (d, $^{2}J_{PC}$ = 13 Hz), 128.5 (s), 128.4 (d, $^{4}J_{PC}$ = 2 Hz), 120.2 (d, $^{1}J_{PC}$ = 89 Hz), 110.0 (d, $^{1}J_{PC}$ = 82 Hz), 12.2 (d, $^{1}J_{PC}$ = 58 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 12.9 (s). Anal. Calcd for $C_{21}H_{20}BrP$: C, 65.81; H, 5.26. Found: C, 65.67; H, 5.36.

(b) Synthesis of (*Z*)-2a. The complex [Pd(dba)$_2$] (288 mg, 0.500 mmol) and (*Z*)-[PhCH=CHPMePh$_2$]$^+$Br$^-$ (192 mg, 0.500 mmol) were dissolved in CH_2Cl_2 (10 mL), and PMePh$_2$ (100 mg, 0.500 mmol) was added at room temperature. The mixture was stirred for 1 h, and filtered through a Celite pad, and the filtrate was concentrated to dryness under reduced pressure. The residue was extracted three-times with a mixed solvent of THF (2 mL) and Et_2O, and the combined extract was concentrated to dryness to give a pale yellow solid of (*Z*)-**2a**. This product was purified three-times by reprecipitation from CH_2Cl_2/Et_2O (1/15 mL) at –78 °C, and then by recrystallization from CH_2Cl_2/Et_2O at –20 °C (162 mg, 47% yield). Mp: 117–119 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.87–7.80, 7.71–7.64, 7.64–7.45, and 7.31–7.20 (m, 20H in total), 6.81 (d, $^{3}J_{HH}$ = 7.0 Hz, 2H), 6.76 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.57 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H), 4.51 (ddd, $^{2}J_{HP}$ = 27.3 Hz, $^{3}J_{HH}$ = 10.7 Hz, $^{3}J_{HP}$ = 5.3 Hz, 1H), 2.87 (ddd, $^{3}J_{HP}$ = 11.9 Hz, $^{3}J_{HH}$ = 10.7 Hz, $^{3}J_{HP}$ = 8.1 Hz, 1H), 2.58 (d, $^{2}J_{HP}$ = 13.6 Hz, 3H), 1.71 (d, $^{2}J_{HP}$ = 6.1 Hz,

3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 142.7 (dd, $^3J_{PC}$ = 7 Hz, $^3J_{PC}$ = 1 Hz), 139.0 (d, $^1J_{PC}$ = 29 Hz), 138.8 (d, $^1J_{PC}$ = 29 Hz), 133.9 (d, $^3J_{PC}$ = 10 Hz), 133.2 (d, $^2J_{PC}$ = 16 Hz), 133.1 (d, $^3J_{PC}$ = 14 Hz), 133.0 (s), 132.9 (d, $^2J_{PC}$ = 16 Hz), 131.0 (s), 131.0 (s), 129.6 (d, $^2J_{PC}$ = 12 Hz), 129.3 (d, $^5J_{PC}$ = 1 Hz), 129.1 (s), 129.1 (d, $^2J_{PC}$ = 12 Hz), 128.4 (d, $^3J_{PC}$ = 9 Hz), 128.4 (d, $^3J_{PC}$ = 9 Hz), 127.3 (s), 126.9 (dd, $^1J_{PC}$ = 80 Hz, $^4J_{PC}$ = 7 Hz), 125.9 (dd, $^1J_{PC}$ = 84 Hz, $^4J_{PC}$ = 4.3 Hz), 125.5 (s), 60.9 (s), 32.3 (dd, $^1J_{PC}$ = 78 Hz, $^2J_{PC}$ = 38 Hz), 16.6 (dd, $^1J_{PC}$ = 66 Hz, $^4J_{PC}$ = 2 Hz), 15.2 (d, $^1J_{PC}$ = 15 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 17.5 (d, $^3J_{PP}$ = 9 Hz), 6.1 (d, $^3J_{PP}$ = 9 Hz). Anal. Calcd for $C_{34}H_{33}BrPPd$: C, 59.19; H, 4.82. Found: C, 58.75; H, 4.92.

P–C Reductive Elimination and Oxidative Addition. A typical procedure is as follows. (*E*)-**1a** (20.7 mg, 0.030 mmol) and 1,3,5-trimethoxybenzene (2.5 mg, 0.015 mmol; internal standard) were placed in an NMR sample tube, and dissolved in CD_2Cl_2 (total 0.6 mL) at room temperature under an argon atmosphere. The sample tube was placed in an NMR sample probe controlled to 40.0 ± 0.1 °C. The reaction was examined at intervals by ^1H NMR spectroscopy using the following marker signals: (*E*)-**1a** (δ 2.07, PMe), (*E*)-**2a** (δ 2.83, PMe), (*E*)-**3a** (d 1.18, PMe), *trans*-[$PdBr_2(PMePh_2)_2$] (δ 2.24, PMe).

The complex [Pd{η^2-(*E*)-PhCH=CHPMePh_2}($PMePh_2$)$_2$]Br ((*E*)-**3a**) was independently prepared from (*E*)-**2a** and $PMePh_2$ (1 equiv) in CD_2Cl_2, and characterized by NMR spectroscopy. ^1H NMR (CD_2Cl_2): δ 7.81–7.21, 7.20–7.05, 6.73–6.67, and 6.67–6.55 (m, 35H in total), 3.74–3.58 (m, 2H), 1.98 (d, $^2J_{HP}$ = 13.1 Hz, 3H), 1.59 (d, $^2J_{HP}$ = 4.9 Hz, 3H), 1.12 (d, $^2J_{HP}$ = 6.1 Hz, 3H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 21.4 (br), 4.5 (br), 4.2 (br). The formation of (*E*)-**3a** took place instantly at room temperature, as already documented for (*E*)-**3b**.[12]

Synthesis and P–C Reductive Elimination of [Pd{CH=CHPh-(*E*)}($PMePh_2$)$_3$]OTf ((*E*)-5a). Complex (*E*)-**1a** (27.6 mg, 0.0400 mmol), $PMePh_2$ (8.0 mg, 0.040 mmol), and 1,3,5-trimethoxybenzene (3.4 mg, 0.020 mmol; internal standard) were dissolved in CD_2Cl_2 (0.75 mL), and AgOTf (10.3 mg, 0.400 mmol) was added at –30 °C. The solution was stirred at this temperature for 1 h to precipitate an off-white powder of AgBr. The orange supernatant was transferred by cannulation to an NMR sample tube, and analyzed by ^1H NMR

spectroscopy at –30 °C, showing the formation of (*E*)-**5a** (96%) and a small amount of [Pd{η^2-(*E*)-PhCH=CHPMePh$_2$}(PMePh$_2$)$_2$]OTf ((*E*)-**6a**) (3%). At 40 °C, (*E*)-**5a** was converted to (*E*)-**6a** within 4 min in 95% selectivity. Since (*E*)-**5a** was thermally too unstable to be isolated, its characterization was carried out by NMR spectroscopy.

(*E*)-5a. ^{1}H NMR (CD_2Cl_2, –30 °C): δ 7.46–7.15 and 7.02–6.92 (m, 33H in total), 6.29 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 6.14 (tdd, $^3J_{HP}$ = 20.6 Hz, $^3J_{HH}$ = 16.6 Hz, $^3J_{HP}$ = 10.5 Hz, 1H), 5.72 (dd, $^3J_{HH}$ = 16.6 Hz, $^4J_{HP}$ = 10.2 Hz, 1H), 1.66 (virtual triplet, J = 3.1 Hz, 6H), 1.30 (t, $^2J_{HP}$ = 7.2 Hz, 3H). ^{31}P{^{1}H} NMR (CD_2Cl_2, –30 °C): δ 7.9 (d, $^2J_{PP}$ = 35 Hz), –0.53 (t, $^2J_{PP}$ = 35 Hz).

(*E*)-6a. ^{1}H NMR (CD_2Cl_2): δ 7.82–7.76, 7.70–7.56, 7.52–7.23, 7.16–7.10, 6.72–6.66, and 6.66–6.56 (m, 35H in total), 3.72–3.51 (m, 2H), 1.85 (d, $^2J_{HP}$ = 13.1 Hz, 3H), 1.57 (d, $^2J_{HP}$ = 5.3 Hz, 3H), 1.12 (d, $^2J_{HP}$ = 6.1 Hz, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 142.1 (dd, $^3J_{PC}$ = 12 Hz, $^3J_{PC}$ = 7 Hz), 138.5 (dd, $^1J_{PC}$ = 29 Hz , $^3J_{PC}$ = 3 Hz), 137.5 (dd, $^1J_{PC}$ = 31 Hz , $^3J_{PC}$ = 3 Hz), 136.8 (dd, $^1J_{PC}$ = 30 Hz , $^3J_{PC}$ = 1 Hz), 134.5 (d, $^4J_{PC}$ = 3 Hz), 134.4 (d, $^4J_{PC}$ = 3 Hz), 134.4 (dd, $^1J_{PC}$ = 31 Hz , $^3J_{PC}$ = 2 Hz), 133.0 (d, $^3J_{PC}$ = 10 Hz), 132.6 (d, $^3J_{PC}$ = 10 Hz), 132.6 (d, $^2J_{PC}$ = 14 Hz), 132.3 (d, $^2J_{PC}$ = 14 Hz), 131.7 (d, $^2J_{PC}$ = 14 Hz), 131.2 (d, $^2J_{PC}$ = 13 Hz), 130.7 (d, $^4J_{PC}$ = 1 Hz), 130.3 (d, $^2J_{PC}$ = 12 Hz), 130.2 (s), 130.1 (d, $^2J_{PC}$ = 12 Hz), 129.6 (d, $^4J_{PC}$ = 1 Hz), 129.4 (d, $^3J_{PC}$ = 9 Hz), 129.4 (d, $^3J_{PC}$ = 9 Hz), 129.2 (m), 128.8 (d, $^3J_{PC}$ = 9 Hz), 128.7 (d, $^3J_{PC}$ = 9 Hz), 126.2 (m), 125.2 (m), 124.6 (dd, $^1J_{PC}$ = 89 Hz, $^3J_{PC}$ = 2 Hz), 124.4 (dd, $^1J_{PC}$ = 83 Hz, $^3J_{PC}$ = 5 Hz), 121.6 (q, $^1J_{FC}$ = 321 Hz), 65.7 (dd, $^2J_{PC}$ = 31 Hz, $^2J_{PC}$ = 5 Hz), 34.0 (ddd, $^1J_{PC}$ = 79 Hz, $^2J_{PC}$ = 32 Hz, $^2J_{PC}$ = 7 Hz), 15.1 (d, $^1J_{PC}$ = 19 Hz), 13.0 (d, $^1J_{PC}$ = 20 Hz), 11.6 (d, $^1J_{PC}$ = 64 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 21.3 (d, $^2J_{PP}$ = 12 Hz), 4.4 (s), 4.1 (d, $^2J_{PP}$ = 12 Hz).

X-ray Structural Analysis. Single crystals of (*E*)-**1a**, (*Z*)-**1a**, (*E*)-**2a**, and (*Z*)-**2a** were grown by slow diffusion of Et_2O into CH_2Cl_2 solutions at –20 °C ((*E*)-**1a**, (*E*)-**2a**, (*Z*)-**2a**) and –30 °C ((*Z*)-**1a**), respectively. The intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo *K*a radiation (λ = 0.71070 Å). The intensity data were collected at 173 K and corrected for Lorentz and polarization effects and for

absorption. The structures were solved by heavy atom Patterson methods (PATTY), expanded using Fourier techniques (DIRDIF99),[19] and refined on F^2 for all reflections (SHELXL-97).[20] All non-hydrogen atoms were refined anisotropically. The H(1) atom of (*Z*)-**1a** was located from a differential Fourier map and refined isotropically. The other hydrogen atoms were placed using AFIX instructions. Crystal data and details of data collection and refinement are summarized in Table 5 and 6.

Computational Details. All calculations were performed using B3LYP level of density functional theory.[21] The Pd atom was described using LANL2DZ basis set including a double-ζ basis set with the Hay and Wadt effective core potential (ECP).[22] The 6-31G(d) basis set was used for other atoms.[23] Diffuse function was added for Br atom. Frequency calculations were carried out to identify all the stationary states as minima (zero imaginary frequencies). All calculations in this study have been performed without any symmetry constraints using the Gaussian 03.[24] The solvent effect was taken into account through single-point calculations at each optimized geometry in vacuo using the polarized continuum model (PCM) at 298.15 K.[25] The partial atomic charges were calculated on the basis of natural bond orbital (NBO) analyses.[26]

Table 5. Crystal Data and Details of the Structure Determination for **1a**

	(*E*)-**1a**	(*Z*)-**1a**
formula	$C_{34}H_{33}BrP_2Pd$	$C_{34}H_{33}BrP_2Pd$
fw	689.85	689.85
crystal size (mm)	0.40 × 0.20 × 0.10	0.28 × 0.20 × 0.08
crystal system	triclinic	monoclinic
a (Å)	7.263(3)	19.196(6)
b (Å)	10.521(4)	16.509(5)
c (Å)	20.015(8)	20.194(7)
α (deg)	85.512(12)	90
β (deg)	86.222(12)	111.543(4)
γ (deg)	79.225(11)	90
V (Å^3)	1495.9(10)	5952(3)
d_{calcd} (cm^{-3})	1.532	1.540
space group	*P*(–1) (#2)	$P2_1/c$ (#14)
Z	2	8
μ (mm^{-1})	2.085	2.095
transmission factors	0.4894–0.8186	0.5915–0.8503
absorption correction	numerical	numerical
θ range (deg)	3.09–27.48	3.06–27.48
no. of reflns collected	12140	46439
no. of unique reflns	6577 (R_{int} = 0.0340)	13534 (R_{int} = 0.0642)
no. of reflns with $I > 2\sigma(I)$	5758	10727
no. of variables (restrains)	345 (0)	693 (0)
GOF on F^2	1.061	0.930
final *R* indices ($I > 2\sigma(I)$)	R_1 = 0.0298, wR_2 = 0.0747	R_1 = 0.0498, wR_2 = 0.1305
R indices (all data)	R_1 = 0.0361, wR_2 = 0.0784	R_1 = 0.0732, wR_2 = 0.1496
max and min peak (e Å^{-3})	0.806, –0.823	1.158, –0.515

Table 6. Crystal Data and Details of the Structure Determination for **2a**

	(*E*)-**2a**	(*Z*)-**2a**
formula	$C_{34}H_{33}BrP_2Pd$	$C_{34}H_{33}BrP_2Pd$
fw	689.85	689.85
crystal size (mm)	0.28 × 0.19 × 0.18	0.08 × 0.05 × 0.01
crystal system	monoclinic	triclinic
a (Å)	9.7501(19)	9.097(3)
b (Å)	25.206(5)	11.925(4)
c (Å)	12.916(2)	14.187(5)
α (deg)	90	77.931(12)
β (deg)	109.107(3)	84.226(13)
γ (deg)	90	80.528(12)
V (Å^3)	2999.4(10)	1480.9(9)
d_{calcd} (cm^{-3})	1.523	1.547
space group	*C*c (#9)	*P*(–1) (#2)
Z	4	2
μ (mm^{-1})	2.079	2.106
transmission factors	0.5936–0.7060	0.6781–0.6781
absorption correction	numerical	empirical
θ range (deg)	3.23–27.48	3.08–27.48
no. of reflns collected	12140	12141
no. of unique reflns	5855 (R_{int} = 0.0267)	6521 (R_{int} = 0.0541)
no. of reflns with $I > 2\sigma(I)$	4546	4103
no. of variables (restrains)	338 (2)	345 (0)
GOF on F^2	1.048	1.059
final *R* indices ($I > 2\sigma(I)$)	R_1 = 0.0496, wR_2 = 0.1335	R_1 = 0.0545, wR_2 = 0.0898
R indices (all data)	R_1 = 0.0586, wR_2 = 0.1374	R_1 = 0.1015, wR_2 = 0.1121
max and min peak (e Å^{-3})	0.984, –0.900	1.099, –0.865

References and notes

(1) (a) Ozawa, F. In *Current Methods in Inorganic Chemistry Volume 3, Fundamentals of Molecular Catalysis*; Yamamoto, A., Kurosawa, H., Eds.; Elsevier Science: Amsterdam, The Netherlands, 2003; Chapter 9. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; John Wiley & Sons: Hoboken, NJ, 2005; pp 55–60. (c) Yamamoto, A. *Organotransition Metal Chemistry, Fundamental Concepts and Application*; John Wiley & Sons: New York, NY, 1986; pp 240–245. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 323–353. (e) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031–1046.

(2) (a) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131–209. (b) Hartwig, J. F. *Inorg. Chem.* **2007**, *46*, 1936–1947. (c) Hartwig, J. F. *Nature* **2008**, *455*, 314–322.

(3) (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) Herrmann, W. A.; Broßmer, C.; Priermeier, T.; Öefele, K. *J. Organomet. Chem.* **1994**, *481*, 97–108. (e) Segelstein, B. E.; Bulter, T. W.; Chenard, B. L. *J. Org. Chem.* **1995**, *60*, 12–13. (f) Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **1995**, 1101–1102. (g) Vicente, J.; Abad, J.-A.; Martinez-Viviente, E.; Ramirez de Arellano, M. C.; Jones, P. G. *Organometallics* **2000**, *19*, 752–760. (h) Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, *22*, 555–562. (i) Hwang, L. K.; Na, Y.; Lee, J.; Do, Y.; Chang, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 6166–6169. (j) Macgregor, S. A. *Chem. Soc. Rev.* **2007**, *36*, 67–76.

(4) (a) Migita, T.; Shimizu, T.; Asami, Y.; Shiobara, J.; Kato, Y.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1385–1389. (b) Migita, T.; Nagai, T.; Kiuchi, K.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2869–2870. (c) Clark, J. H.; Tavener, S. J.; Barlow, S. J. *J. Mater. Chem.* **1995**, *5*, 827–830. (d) Vicente, J.; Abad, J.-A.; Frankland, A. D.; De Arellano, M. C. R. *Chem. Eur. J.* **1999**, *5*, 3066–3075. (e) Bourgogne, C.; Le F., Y.;

Juen, P.; Masson, P.; Nicoud, J.-F.; Masse, R. *Chem. Mater.* **2000**, *12*, 1025–1033. (f) Lambert, C.; Gaschler, W.; Noll, G.; Weber, M.; Schmalzlin, E.; Brauchle, C.; Meerholz, K. *J. Chem. Soc., Perkin Trans. 2* **2001**, *6*, 964–974. (g) de la Torre, G.; Gouloumis, A.; Vazquez, P.; Torres, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2895–2898. (h) Cheng, Z.; Subbarayan, M.; Chen, X.; Gambhir, S. S. *J. Label. Compd. Radiopharm.* **2005**, *48*, 131–137. (i) Marcoux, D.; Charette, A. B. *J. Org. Chem.* **2008**, *73*, 590–593.

(5) (a) Huang, C.-C.; Duan, J.-P.; Wu, M.-Y.; Liao, F.-L.; Wang, S.-L.; Cheng, C.-H. *Organometallics* **1998**, *17*, 676–682. (b) Rybin, L. V.; Petrovskaya, E. A.; Rubinskaya, M. I.; Kuz'mina, L. G.; Struchkov, Y. T.; Kaverin, V. V.; Koneva, N. Y. *J. Organomet. Chem.* **1985**, *288*, 119–129. (c) Kowalski, M. H.; Hinkle, R. J.; Stang, P. J. *J. Org. Chem.* **1989**, *54*, 2783–2784. (d) Hinkle, R. J.; Stang, P. J.; Kowalski, M. H. *J. Org. Chem.* **1990**, *55*, 5033–5036. (e) Dervisi, A.; Edwards, P. G.; Newman, P. D.; Tooze, R. P. *Dalton* **2000**, 523–528. (f) Arisawa, M.; Yamaguchi, M. *J. Am. Chem. Soc.* **2000**, *122*, 2387–2388. (g) Jutand, A.; Negri, S. *Organometallics* **2003**, *22*, 4229–4237.

(6) (a) Arisawa, M.; Yamaguchi, M. *J. Am. Chem. Soc.* **2006**, *128*, 50–51. (b) Arisawa, M.; Yamaguchi, M. *Adv. Synth. Cat.* **2001**, *343*, 27–28.

(7) (a) Kwong, F. Y.; Chan, K. S. *Organometallics* **2000**, *19*, 2058–2060. (b) Kwong, F. Y.; Chan, K. S. *Chem. Commun.* **2000**, 1069–1070. (c) Kwong, F. Y.; Lai, C. W.; Tian, Y.; Chan, K. S. *Tetrahedron Lett.* **2000**, *41*, 10285–10289. (d) Kwong, F. Y.; Chan, K. S. *Organometallics* **2001**, *20*, 2570–2578. (e) Lai, C. W.; Kwong, F. Y.; Wang, Y.; Chan, K. S. *Tetrahedron Lett.* **2001**, *42*, 4883–4885. (f) Kwong, F. Y.; Lai, C. W.; Chan, K. S. *Tetrahedron Lett.* **2002**, *43*, 3537–3539. (g) Kwong, F. Y.; Lai, C. W.; Yu, M.; Tian, Y.; Chan, K. S. *Tetrahedron* **2003**, *59*, 10295–10305. (h) Kwong, F. Y.; Lai, C. W.; Yu, M.; Chan, K. S. *Tetrahedron* **2004**, *60*, 5635–5645. (i) Wang, Y.; Lai, C. W.; Kwong, F. Y.; Jia, W.; Chan, K. S. *Tetrahedron* **2004**, *60*, 9433–9439.

(8) An alternative mechanism involving a phosphido intermediate has been proposed for the conversion of *trans*-[$PdMe(I)(PPh_3)_2$] to [$PdPh(I)(PMePh_2)(PPh_3)$]: Morita, D. K.; Stille, J. K.; Norton, J. R. *J. Am. Chem. Soc.* **1995**, *117*, 8576–8581.

(9) The mechanism of P–C reductive elimination of anionic phosphorus ligands such as phosphido and phosphonato has been examined using isolated complexes: (a) Gaumont, A.-C.; Brown, J. M.; Hursthouse, M. B.; Coles, S. J. *Chem. Commun.* **1999**, 63–64. (b) Adam M.; Stockland, R. A., Jr.; Clark, R.; Guzei, I. *Organometallics* **2002**, *21*, 3278–3284. (c) Stockland, R. A., Jr.; Levine, A. M.; Giovine, M. T.; Guzei, I. A.; Cannistra, J. C. *Organometallics* **2004**, *23*, 647–656. (d) Kohler, M. C.; Stockland, R. A., Jr.; Rath, N. P. *Organometallics* **2006**, *25*, 5746–5756. (e) Kalek, M.; Stawinski, J. *Organometallics* **2008**, *27*, 5876–5888.

(10) The P–C reductive elimination of styryl complex has been reported for *trans*-[Pd{CH=CHPh-(*E*)}Br(PPh_3)$_2$] (**1b**).[5a]

(11) Chapter 3 of this thesis: Wakioka, M.; Nagao, M.; Ozawa, F. *Organometallics* **2008**, *27*, 602–608.

(12) The PPh_3 analogue [Pd{η^2-(*E*)-PhCH=CHPPh_3}(PPh_3)$_2$]Br ((*E*)-**3b**) has been reported.[5a]

(13) A metallophosphorane intermediate has been proposed for F/Ph exchange of [RhF(PPh_3)$_3$] affording [RhPh($PFPh_2$)(PPh_3)$_2$]: Macgregor, S. A.; Roe, D. C.; Marshall, W. J.; Bloch, K. M.; Bakhmutov, V. I.; Grushin, V. V. *J. Am. Chem. Soc.* **2005**, *127*, 15304-15321.

(14) (a) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174–4181. (b) Brown, J. M.; Cooley, N. A. *Organometallics* **1990**, *9*, 353–359. (c) Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431–1438. (d) Ozawa, F.; Tani, T.; Katayama, H. *Organometallics* **2005**, *24*, 2511–2515.

(15) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220–223.

(16) Dolby, L. J.; Wilkins, C.; Frey, T. G. *J. Org. Chem.* **1966**, *31*, 1110–1116.

(17) Taillefer, M.; Cristau, H. J.; Fruchier, A.; Vicente, V. *J. Organomet. Chem.* **2001**, *624*, 307–315.

(18) Ukai, T.; Kawamura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, 65, 253–266.

(19) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; García-Grana, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. *The DIRDIF99 Program System*; University of Nijmegen: The Netherlands, 1999.

(20) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Germany, 1997.

(21) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(22) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284–298.

(23) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654–3665.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Gaussian, Inc., Pittsburgh, PA, 2004.

(25) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117–119. (b) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027–2094. (c) Tomasi, J.; Cammi, R. *J. Comput. Chem.* **1995**, *16*, 1449–1458.

(25) Glendening, E. D.; Read, A. E.; Carpenter, J. E.; Weinhold, F. *NBO* (version 3.1); Gaussian, Inc., Pittsburgh, PA, 2004.

Chapter 5

Stereocontrolled Synthesis and Photo-induced Insolubilization of All-trans Poly(arylenevinylene)s

Abstract

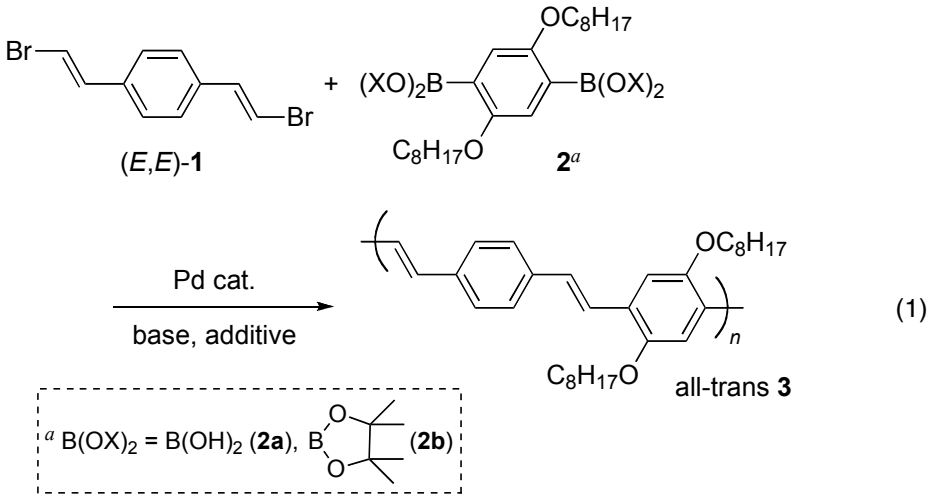
To achieve highly selective synthesis of all-trans poly[(*p*-phenylenevinylene)--*alt*-(2,5-dioctyloxy-1,4-phenylenevinylene)]s (**3**) by Suzuki–Miyaura-type polycondensation of (*E*,*E*)-1,4-bis(2-bromoethenyl)benzene (**1**) and 2,5-dioctyloxybenzene-1,4-diboronic acid (**2**), appropriate catalytic conditions have been investigated using (*E*)-styryl bromide (**4**) and 2,5-dioctyloxybenzeneboronic acid (**5**) as model compounds of **1** and **2**, respectively. The reaction of **4** and **5** in toluene in the presence of $[Pd(PPh_3)_4]$ catalyst and aqueous K_2CO_3 base affords considerable amounts of homo-coupling products (i.e., 1,4-diphenylbutadiene (13%) and 2,2'-5,5'-tetraoctyloxybiphenyl (22%)), together with (*E*)-2,5-dioctyloxystilbene (**6**) as the cross-coupling product (30%). The amounts of homo-coupling products are reduced effectively by using aqueous NaOH as a base and Bu_4NBr as a phase-transfer catalyst. Moreover, the use of $[Pd(PBu^t_3)_2]$ instead of $[Pd(PPh_3)_4]$ leads to almost perfect selectivity of **6** under mild conditions. Hence the desired all-trans **3** has been successfully prepared without notable defects in the polymer chain. Photochemical properties of all-trans **3** in thin films are described.

Introduction

Poly(phenylenevinylene)s (PPVs) and their homologues (i.e., poly(arylenevinylene)s: PAVs) are among the π-conjugated polymers that have wide application in optoelectronic and biological devices such as light-emitting diodes (LEDs),[1,2] photovoltaic devices,[3] plastic lasers,[4] and field-effect transistors (FETs).[5] They have been synthesized by a variety of methods, including thermolysis of sulfonium polymer precursors (Wessling),[6] dehydrohalogenative polycondensation of bis(halomethyl)benzenes (Gilch),[7] Wittig–Horner-type polycondensation of diphosphonates with phthaldehydes,[8] ring-opening metathesis polymerization (ROMP),[9] acyclic diene metathesis (ADMET),[10] and palladium-catalyzed polycondensations using cross-coupling reactions (Mizoroki–Heck,[11] Migita–Kosugi–Stille,[12] and Hiyama[13,14]), and most of them afford all-trans or trans-rich PAVs having *trans*-vinylene linkages. On the other hand, our research group has recently reported that all-cis PAVs having the vinylene linkages entirely controlled to cis geometry are successfully prepared by Suzuki–Miyaura-type polycondensation of (*Z*,*Z*)-bis(2-bromoethenyl)arenes with 2,5-dioctyloxybenzene-1,4-diboronic acid.[15] It has also been found that all-cis PAVs thus prepared exhibit unique photochemical properties; namely, the polymers undergo one-way photoisomerization to all-trans isomers in thin films, and the resulting films become much less soluble than before photo-irradiation.[15a] This phenomenon (i.e., photo-induced insolubilization) should be useful for fabricating multilayered devices of π-conjugated polymers by solution processes.[16]

In Chapter 1, the author investigated this phenomenon using all-cis poly(*p*-phenylenevinylene)s (PpPVs) in detail, and found that the photo-induced insolubilization is significantly facilitated when the polymers bear a 2-bromoethenyl group at the chain end, which is derived from (*Z*,*Z*)-bis(2-bromoethenyl)benzene as a substrate of Suzuki–Miyaura-type polycondensation. Thus, although the insolubilization in thin films have so far been observed only for all-cis PpPVs, and all-trans PpPV independently prepared by Hiyama-type polycondensation does not show this phenomenon,[17] there is a possibility that all-trans PpPVs with the same

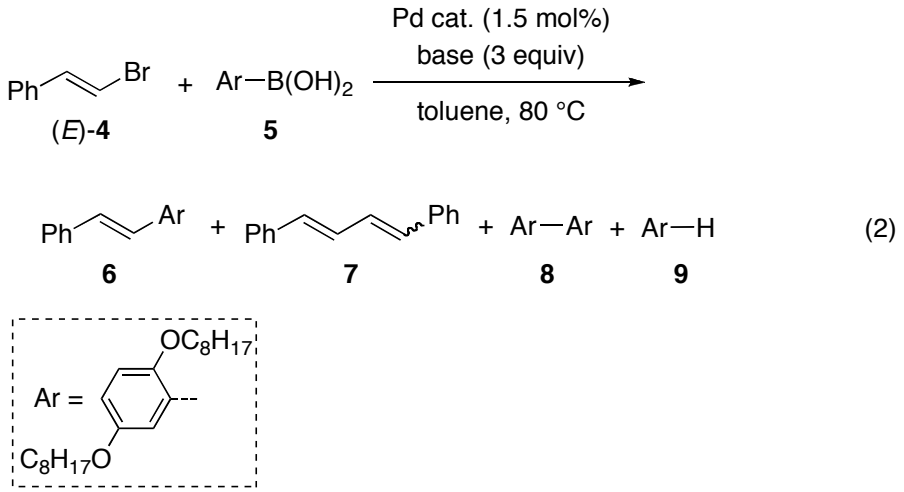
terminal structures are insolubilized by UV-irradiation as well. Accordingly, the author prepared all-trans PpPVs (**3**) via Suzuki–Miyaura-type polycondensation of (*E*,*E*)-1,4-bis(2-bromoethenyl)benzene (**1**) with 2,5-dioctyloxybenzene-1,4-diboronic acid (**2**) (eq 1), and examined their photochemical properties in thin films.



(1)

Results and Discussion

Examination of Catalytic Conditions. As demonstrated in Chapter 3, unlike the reaction of (*Z*)-styryl bromide, the Suzuki–Miyaura cross-coupling of (*E*)-styryl bromide with $PhB(OH)_2$ is very prone to compete with homo-coupling giving 1,4-diphenylbutadiene and biphenyl. Because the homo-coupling reaction causes defects in polymer chains upon polycondensation, a highly selective system for cross-coupling was pursued by using (*E*)-styryl bromide (**4**) and 2,5-dioctyloxybenzeneboronic acid (**5**) as the model compounds of (*E*,*E*)-**1** and **2** in eq 1, respectively (eq 2). Table 1 summarizes the results. The reaction of (*E*)-**4** with **5** in toluene at 80 °C in the presence of $[Pd(PPh_3)_4]$ (1.5 mol%) and aqueous K_2CO_3 (3 equiv) afforded four kinds of products; i.e., cross-coupling product **6** (30%), homo-coupling products **7** (13%) and **8** (22%), and a trace amount of 1,4-dioctyloxybenzene (**9**), formed by hydrolysis of **5** (entry 1).



It is accepted that the Suzuki–Miyaura reaction proceeds via three elementary processes.[18] As for the reaction of eq 2, the first step is the oxidative addition of (*E*)-**4** to a palladium(0) species $[Pd(PR_3)_n]$ (process (i)). The resulting $[Pd(CH{=}CHPh)(Br)(PR_3)_2]$ undergoes transmetalation with **5** with the aid of a base to give $[Pd(CH{=}CHPh)(Ar)(PR_3)_2]$ (process (ii)), which reductively eliminates **6** (process (iii)). The homo-coupling process competes with the transmetalation process (ii). In Chapter 3, the author confirmed that the

homo-coupling product **7** is afforded by the reaction of [Pd(CH=CHPh)Br(PR_3)$_2$] with (*E*)-**4**. Moreover, [$PdBr_2(PR_3)_2$] generated concurrently with **7** in the system reacts with **5** in the presence of a base to give **8**. Interestingly, the formation of **7** is catalyzed by [Pd(η^2-PhCH=CHPR_3)Br(PR_3)], which is provided from [Pd(CH=CHPh)Br(PR_3)$_2$] by P–C reductive elimination of the styryl and phosphine ligands. Taking these mechanistic findings into consideration, the author examined the catalytic conditions to facilitate the transmetalation process, compared with the homo-coupling process.

First, the reaction was examined using a variety of bases (entries 1–8). It has been known that the association with a base is essential for the areneboronic acid to gain the nucleophilicity required for the transmetalation.[18] Actually, aqueous NaOH as a strong base notably enhanced the reactivity and selectivity for cross-coupling (entry 4), while aqueous KOH was not so effective (entry 5). The other bases including metal carbonates (entries 1 and 2), phosphate (entry 3), and fluorides (entries 6 and 7) were much less effective, and silver oxide mainly caused hydrolysis of **5** to give **9** (entry 8). The reactivity and selectivity of the reactions using aqueous NaOH and KOH bases were greatly improved by addition of Bu_4NBr or $(Octyl)_3MeNCl$ to the system (entries 9–11). It is reasonable that the ammonium salts, serving as a phase-transfer catalyst in a two-phase system consisting of toluene and water, enhance the efficiency of a base, thereby facilitating the transmetalation process. The combination of aqueous NaOH and Bu_4NBr was particularly effective, giving a quantitative yield of **6** (entry 9).

Next, basic and bulky tertiary phosphine ligands were examined as another approach to a highly selective system for the cross-coupling of (*E*)-styryl bromide (**4**) and areneboronic acid (**5**). As described above, the homo-coupling proceeds via a unique reaction process induced by P–C reductive elimination of [Pd(CH=CHPh)Br(PR_3)$_2$] intermediate. As shown in Chapter 4, the P–C reductive elimination is significantly decelerated when the tertiary phosphine ligands are highly basic. The author also anticipated that a bulky ligand provides a highly coordinatively unsaturated species, suitable for transmetalation as a ligand displacement process. As seen from entries 13–16 in Table 1, PCy_3 was insufficient (entry

12), but more bulky PBu^t_3 resulted in almost quantitative yields of **6**, even in the absence of Bu_4NBr (entries 13, 14 and 16). The reaction smoothly proceeded even at room temperature (entry 15).

Table 1. Suzuki–Miyaura Cross-Coupling of (*E*)-**4** and **5**[a]

entry	Pd cat. (1.5 mol%)	base[b] (3 equiv)	additive (1 equiv)	time (h)	yield (%)[c] **6**[d]	**7**[e]	**8**	**9**
1	$[Pd(PPh_3)_4]$	aq K_2CO_3	none	2	30 (97/3)	13 (29/71)	22	<1
2	$[Pd(PPh_3)_4]$	aq Cs_2CO_3	none	2	25 (99/1)	11 (18/82)	18	2
3	$[Pd(PPh_3)_4]$	aq K_3PO_4	none	2	31 (96/4)	11 (22/78)	20	<1
4	$[Pd(PPh_3)_4]$	aq NaOH	none	2	95 (>99/1)	4 (42/58)	4	1
5	$[Pd(PPh_3)_4]$	aq KOH	none	2	72 (98/2)	27 (18/82)	20	4
6	$[Pd(PPh_3)_4]$	aq KF	none	2	20 (98/2)	9 (28/72)	15	2
7	$[Pd(PPh_3)_4]$	aq CsF	none	2	21 (99/1)	10 (22/78)	16	2
8	$[Pd(PPh_3)_4]$	aq Ag_2O	none	2	22 (98/2)	6 (77/23)	4	74
9	$[Pd(PPh_3)_4]$	aq NaOH	Bu_4NBr	1	99 (>99/1)[g]	0	<1	<1
10	$[Pd(PPh_3)_4]$	aq KOH	Bu_4NBr	1	97 (>99/1)	0	1	<1
11	$[Pd(PPh_3)_4]$	aq NaOH	$(Octyl)_3MeNCl$	1	97 (>99/1)	0	3	<1
12	$[Pd(PCy_3)_2]$	aq KOH	none	3	83 (99/1)	10 (16/84)	7	7
13	$[Pd(PBu^t_3)_2]$	aq NaOH	none	1	96 (>99/1)	<1	<1	2
14	$[Pd(PBu^t_3)_2]$	aq KOH	none	1	97 (>99/1)	<1	<1	2
15[f]	$[Pd(PBu^t_3)_2]$	aq NaOH	none	1	98 (>99/1)	0	<1	1
16	$[Pd(PBu^t_3)_2]$	aq NaOH	Bu_4NBr	1	98 (>99/1)[h]	0	<1	1

[a] Reactions were run in a 0.20 mmol scale in toluene (1 mL) at 80 °C unless otherwise noted. [b] All bases were employed as 3 M aqueous solutions. [c] Determined by ^1H NMR spectroscopy using hexamethylbenzene as an internal standard. [d] The (*E*)/(*Z*) ratios of **6** are in parentheses. [e] The (*E*,*E*)/(*E*,*Z*) ratios of **7** are in parentheses. [f] The reaction was run at room temperature. [g] Isolated yield: 98%. [h] Isolated yield: 97%.

Synthesis of All-trans PpPVs. The synthesis of all-trans **3** in eq 1 was carried out under the reaction conditions based on entries 9, 13, and 15 in Table 1 (Table 2). An 1:1 mixture of (*E*,*E*)-1,4-bis(2-bromoethenyl)benzene (**1**) and 2,5-dioctyloxy-benzene-1,4-diboronic acid (**2a**) was heated in toluene at 80 °C for 24 h in the presence of $[Pd(PPh_3)_4]$ (1.5 mol%), aqueous NaOH (3 equiv), and Bu_4NBr (1 equiv), giving orange fluorescent suspension, which was diluted with CH_2Cl_2, washed with H_2O, and reprecipitated in methanol (entry 1). ^{1}H NMR analysis of the resulting polymer revealed a partial diene structure in the main chain (< 5%). On the other hand, the same reaction using $[Pd(PBu^t_3)_2]$ in place of $[Pd(PPh_3)_4]$ afforded all-trans **3** without a notable defect of the PpPV skeleton (entry 2). The molecular weight decreased in the absence of Bu_4NBr (entry 3), but recovered a comparable level of entry 2 when the reaction was carried out at room temperature using boronic acid ester **2b** (entry 4). The reaction was further improved in THF (entry 5), and all-trans **3** with M_n = 9700 was obtained in a quantitative yield under slightly warmed conditions (entry 6). Although the reaction was also examined in a refluxed THF solution, the resulting polymer was insoluble in $CHCl_3$, and therefore could not be fully characterized.

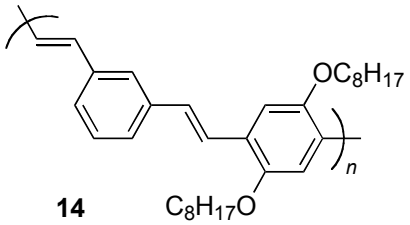
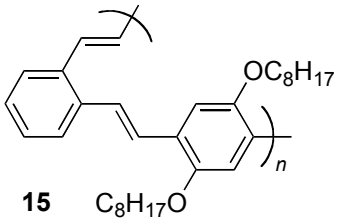
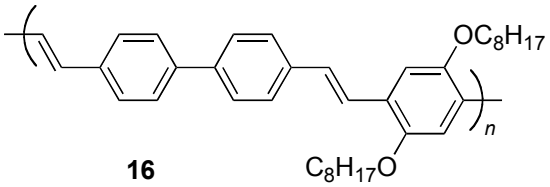
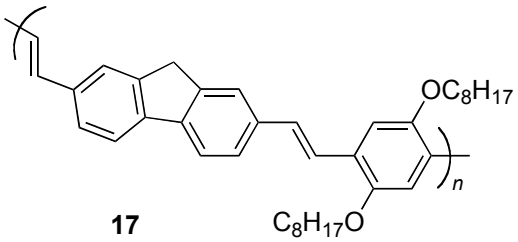
Table 2. Polycondensation of (*E*,*E*)-**1** with **2** [a]

entry	Pd cat.	**2**	Bu_4NBr	solvent	temp (°C)	yield [b] (%)	M_n [c]	M_w/M_n [c]	cis/trans [d]	defect [d]
1	$[Pd(PPh_3)_4]$	**2a**	1 equiv	toluene	80	>99	8400	3.03	<1/99	trace
2	$[Pd(PBu^t_3)_2]$	**2a**	1 equiv	toluene	80	>99	4900	2.48	<1/99	none
3	$[Pd(PBu^t_3)_2]$	**2a**	—	toluene	80	91	2700	1.57	<1/99	none
4	$[Pd(PBu^t_3)_2]$	**2b**	—	toluene	20	98	4100	1.44	<1/99	none
5	$[Pd(PBu^t_3)_2]$	**2b**	—	THF	20	>99	7500	1.80	<1/99	none
6	$[Pd(PBu^t_3)_2]$	**2b**	—	THF	30	>99	9700	1.96	<1/99	none

[a] Reactions were carried out for 24 h using (*E*,*E*)-**1** (0.20 mmol), **2** (0.20 mmol), aqueous NaOH (3.0 M, 0.6 mmol), and Pd catalyst (1.5 mol%) in solution (2.0 mL). [b] Yield of MeOH-insoluble polymer. [c] Determined by GPC calibration based on polystyrene standards. [d] Determined by ^{1}H NMR.

Polycondensation of several (*E*,*E*)-bis(2-bromoethenyl)arenes (**10**–**13**) with **2b** was successful under the optimized catalytic conditions, and thereby four kinds of all-trans PAVs (**14**–**17**) were synthesized without notable structural defects (Table 3).

Table 3. All-trans PAVs prepared by Polycondensation of (*E*,*E*)-BrCH=CH-Ar-CH=CHBr (**10**–**13**) with **2b** [a]

entry	PAV	yield (%) [b]	M_n [c]	M_w/M_n [c]	cis/trans [d]
1	 **14**	>99	18300	2.10	<1/99
2	 **15**	99	9900	2.66	<1/99
3	 **16**	>99	7600	1.44	<1/99
4	 **17**	>99	6900	1.17	<1/99

[a] Reactions were run at 20 °C for 24 h using (*E*,*E*)-**10**–**13** (0.20 mmol), **2b** (0.20 mmol), aqueous NaOH (3.0 M, 0.60 mmol), and [Pd(PBu^t_3)$_2$] (1.5 mol%) in THF (2.0 mL). Ar = *m*-phenylene (**10**), *o*-phenylene (**11**), 4,4'-biphenylene (**12**), 2,7-fluorenylene (**13**). [b] Yield of MeOH-insoluble polymer. [c] Determined by GPC calibration based on polystyrene standards. [d] Determined by ^{1}H NMR.

Characterization of All-trans PpPVs. The polymer structures were characterized by NMR spectroscopy. Figure 1 compares the ^{1}H NMR spectrum of all-trans **3** (A) with that of 4-(2-bromoethenyl)stilbene (**18**) having the presumed terminal structures (B). It has been shown that the stereoregularity of vinylene linkages can be estimated from the peak intensities of the OCH_2 signals of octyloxy groups; the signal of *trans*-PpPV appears at δ 4.08, whereas that of *cis*-isomer at δ 3.54.[15] Thus, no trace of the signal of *cis*-isomer was observed in spectrum (A). As for the terminal structures, the spectrum (A) exhibited the signals assignable to 2,5-dioctyloxyphenyl ((a)–(d)) and (*E*)-2-bromoethenyl (e) groups in reasonable

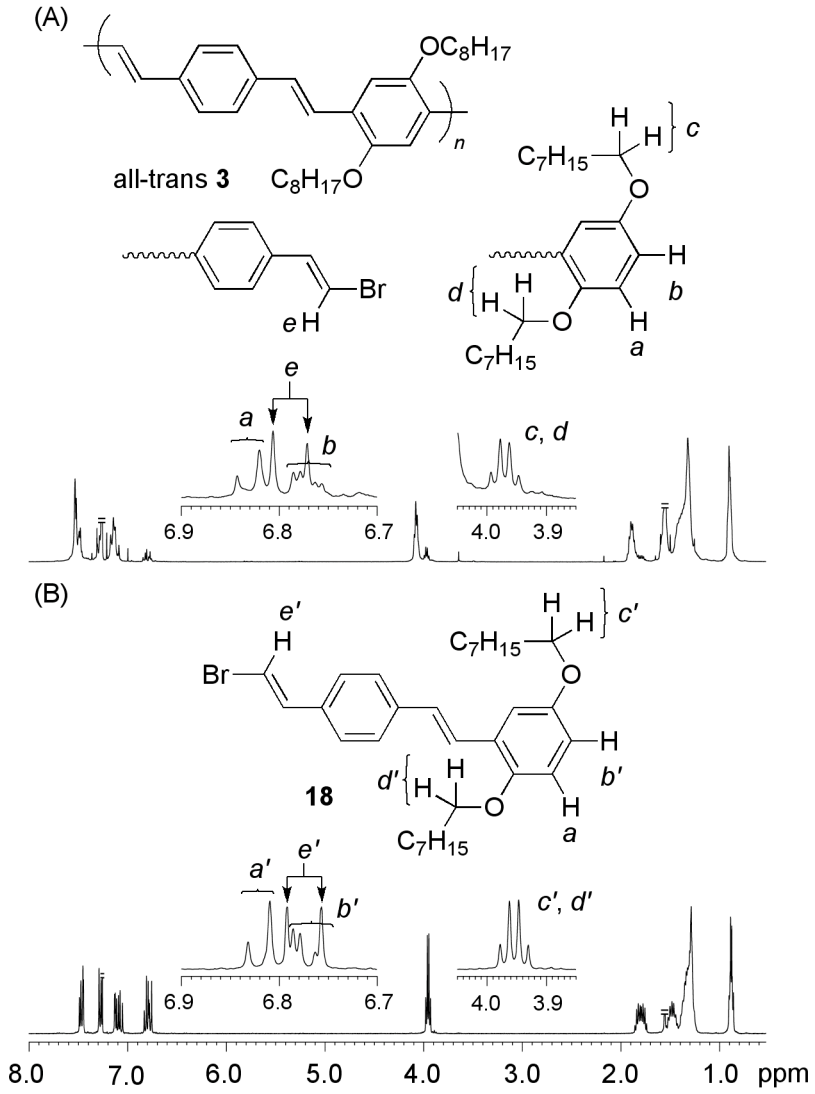


Figure 1. ^{1}H NMR spectra of (A) all-trans **3** (run 2 in Table 2) and (B) 4-(2-bromoethenyl)stilbene (**18**) in $CDCl_3$ at room temperature.

peak intensities. Accordingly, it was concluded that all-trans **3** bears these groups at each terminus.

Photo-induced Insolubilization of All-trans PpPVs. A thin film of all-trans **3** (M_n = 9700, entry 6 in Table 2) was prepared from a $CHCl_3$ solution (2.0 wt%) by spin-coating on a quartz plate ((i) blue line, λ_{max} = 478 nm), irradiated with a Xe lamp (λ = 300–400 nm, 21.0 mW cm^{-2}) for 1 h under vacuum at room temperature ((ii) red line, λ_{max} = 478 nm), and rinsed twice with $CHCl_3$ and dried ((iii) green line). Figure 2 shows the UV-vis spectrum at each step. Unlike all-cis PpPVs described in Chapter 1, no notable change was observed before and after UV-irradiation ((i) and (ii)). However, after rinsing, 43% of PpPV film remained on the substrate (iii). Hence, all-trans **3** having a 2-bromoethenyl group at the polymer end was insolubilized under UV light, while the performance was considerably low as compared with all-cis PpPVs (vide infra). It was confirmed that most part of the polymer dissolves in $CHCl_3$

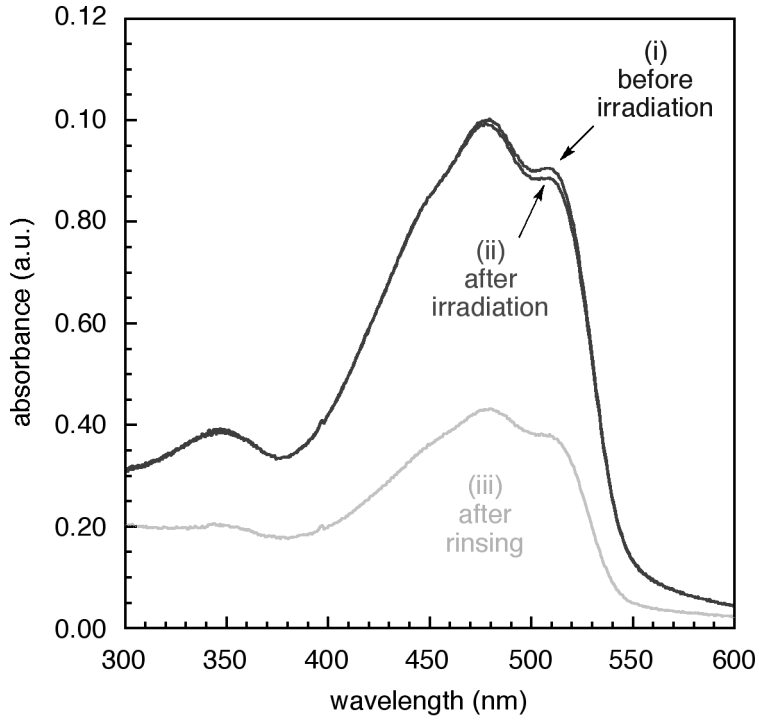


Figure 2. UV–vis absorption spectra of all-trans **3** (M_n = 9700) in thin film, before and after UV-irradiation (i and ii), and after rinsing with $CHCl_3$ (iii).

without UV-irradiation.[19]

Table 4 compares the performance of all-trans and all-cis **3** on photo-induced insolubilization. The data for all-cis **3** are taken from Chapter 1. It is clearly seen that the performance of all-trans **3** is significantly lower than that of all-cis **3**. As pointed out in Chapter 1, all-cis PpPVs are highly mobile molecules in thin films. Accordingly, they may form a highly aligned structure of all-trans PpPVs upon photoisomerization with the aid of attractive interactions between the molecules such as π–π stacking. In contrast, all-trans **3** should be a highly rigid molecule, and thereby unlikely to undergo molecular alignment in thin films. As an indirect support, the thin films of all-trans **3** remained insulators after photo-irradiation, although those of all-cis **3** exhibited the thin film transistor (TFT) mobility (μ_{TFT}) of up to 1.6×10^{-4} cm^2 V^{-1} s^{-1} upon photo-induced insolubilization.

Table 4. Photo-induced Insolubilization of PpPVs

entry	PPV	M_n [a]	M_w/M_n [a]	insolubilized PpPV (%) [b]
1	all-trans **3**	2700	1.57	5
2	all-trans **3**	4100	1.44	10
3	all-trans **3**	7500	1.80	22
4	all-trans **3**	9700	1.96	43
5	all-cis **3**	2800	1.55	33
6	all-cis **3**	4800	2.20	64
7	all-cis **3**	7000	2.69	84
8	all-cis **3**	8100	3.93	89

[a] Determined by GPC calibration based on polystyrene standards. [b] Determined by UV–vis absorption spectroscopy.

Conclusions

The author has succeeded in synthesizing all-trans PpPVs and its homologues bearing a 2-bromoethenyl group at the chain end, using Suzuki–Miyaura-type polycondensation of (*E*,*E*)-bis(2-bromoethenyl)arenes with 2,5-dioctyloxybenzene-1,4-dibronic acid derivatives. Taking the previous mechanistic findings about the homo-coupling of alkenyl bromide into consideration, catalytic cross-coupling systems with perfect selectivity have been developed by pursuit of the reaction conditions. The resulting all-trans PpPVs undergo photo-induced insolubilization, while their performance is much lower than that of all-cis isomers. The present study has provided an additional evidence of the significance of all-cis configuration for the photo-induced insolubilization of PpPV films.

Experimental Section

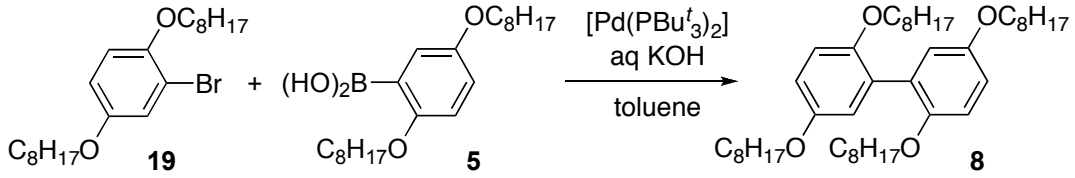
General Considerations. All manipulations using organometallic compounds were carried out under a nitrogen or argon atmosphere using conventional Schlenk techniques. Nitrogen and argon gas were dried by passing through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H NMR 400.13 MHz and ^{13}C NMR 100.62 MHz). Chemical shifts are reported in δ (ppm), referenced to the ^{1}H (residual protons) and ^{13}C signals of deuterated solvents. Mass spectra were measured on a Shimadzu GC-MS QP2010 spectrometer (EI, 70 eV). Melting points were measured with a Yanaco MP-S3 instrument. Analytical GPC was carried out on a JASCO GPC assembly consisting of a model PU-980 precision pump, a model RI-1530 refractive index detector, and three polystyrene gel columns (Shodex KF-801, KF-803L, KF-805L). THF was used as the mobile phase with a flow rate of 1.0 mL min^{-1} at 40 °C. The columns were calibrated against 9 standard polystyrene samples (Shodex; M_n = 980–1920000). Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University. Spin-coating of PPV was performed with a Mikasa spin coater 1H-DX2. Photo-irradiation was carried out at room

temperature with an Asahi Spectra LAX-101 Xe lamp. UV-vis absorption spectra were recorded on a JASCO V-560 spectrometer.

Toluene (Kanto, dehydrated) and THF (Wako, dehydrated) were used as received. The following compounds were synthesized according to literatures: $[Pd(PPh_3)_4]$,[20] $[Pd(PCy_3)_2]$,[21] $[Pd(PBu^t_3)_2]$,[21] $[RuHCl(CO)(PPh_3)_3]$,[22] (*E*)-styryl bromide ((*E*)-**4**),[23] 2,5-dioctyloxybenzeneboronic acid (**5**),[24] 2,5-dioctyloxy-1,4-benzenediboronic acid (**2a**),[25] 1,4-bis(4,4,5,5--tetramethyl-1,3,2-dioxaborolan-2-yl)-2,5-dioctyloxybenzene (**2b**),[15b] 1-bromo-2,5-dioctyloxybenzene (**19**),[24] 4,4'-diethynylbiphenyl (**20c**),[26] and 2,7-diethynylfluorene (**20d**).[27] All other chemicals were obtained from commercial suppliers and used without further purification.

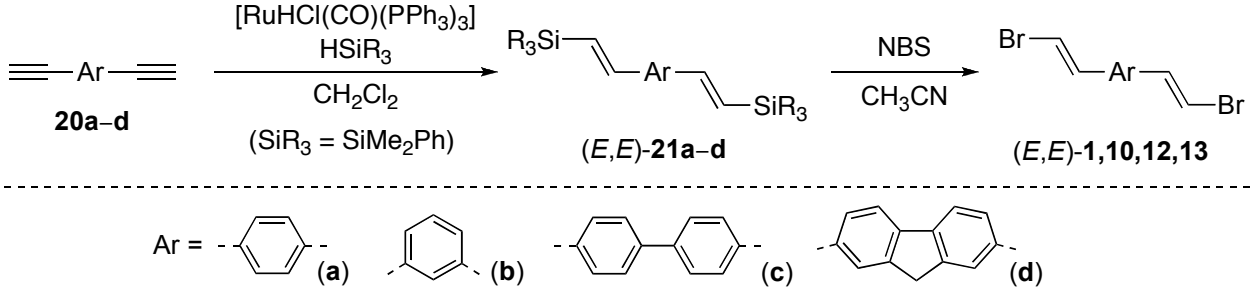
Suzuki–Miyaura Cross-coupling of (*E*)-4 and 5 (run 9 in Table 1). A 10 mL Schlenk tube was charged with **5** (75.7 mg, 0.200 mmol), $[Pd(PPh_3)_4]$ (3.5 mg, 3.0 μmol), Bu_4NBr (64.5 mg, 0.200 mmol), toluene (1 mL), and 3.0 M aqueous NaOH (0.20 mL, 0.60 mmol). To the resulting suspension was added (*E*)-**4** (36.6 mg, 0.200 mmol). The mixture was stirred at 80 °C for 1 h. After cooling to room temperature, the mixture was passed through a short column (SiO_2, hexane/CH_2Cl_2 (1/1)), concentrated to dryness, and examined by ^1H NMR using hexamethylbenzene as an internal standard, showing the formation of (*E*)-2,5-dioctyloxystilbene (**6**, (*E*)/(*Z*) > 99/1) in 99% yield, which was isolated as a colorless oil by column chromatography (SiO_2, hexane and then hexane/CH_2Cl_2 (4/1)) (85.7 mg, 98% yield). The NMR data for (*E*)-**6** were identical to those reported.[28] ^1H NMR ($CDCl_3$): δ 7.52 (d, *J* = 7.5 Hz, 2H, $H^{2,6}$ of C_6H_5), 7.46 (d, *J* = 16.5 Hz, 1H, C_6H_3CH=CH), 7.35 (t, *J* = 7.7 Hz, 2H, $H^{3,5}$ of C_6H_5), 7.24 (t, *J* = 7.5 Hz, 1H, H^4 of C_6H_5), 7.15 (d, *J* = 3.0 Hz, 1H, H^6 of C_6H_3), 7.11 (d, *J* = 16.5 Hz, 1H, C_6H_3CH=C*H*), 6.82 (d, *J* = 8.9 Hz, 1H, H^3 of C_6H_3), 6.77 (dd, *J* = 8.9, 2.9 Hz, 1H, H^4 of C_6H_3), 3.96 (t, *J* = 6.5 Hz, 2H, OCH_2), 3.95 (t, *J* = 6.5 Hz, 2H, OCH_2), 1.87–1.73 (m, 4H, CH_2), 1.54–1.23 (m, 20H, CH_2), 0.93–0.84 (m, 6H, CH_3).

Synthesis of 2,2',5,5'-tetraoctyloxybiphenyl (8).



To a solution of 1-bromo-2,5-dioctyloxybenzene (**19**) (207 mg, 0.500 mmol) and **5** (208 mg, 0.550 mmol) in toluene (5 mL) were successively added $[Pd(PBu^t_3)_2]$ (2.8 mg, 5.0 μmol) and 3.0 M aqueous KOH (0.50 mL, 1.5 mmol). The mixture was stirred at 80 °C for 12 h, and passed through a short column (SiO_2, hexane/CH_2Cl_2 (1/1)) at room temperature. Purification of the crude product by flash column chromatography (SiO_2, hexane and then hexane/CH_2Cl_2 (2/1)) gave the title compound as a white solid (331.6 mg, 99% yield). Mp: 46–48 °C. ^{1}H NMR ($CDCl_3$): δ 6.86 (d, J = 6.3 Hz, 2H, $H^{3,3'}$ of Ar), 6.84 (s, 2H, $H^{6,6'}$ of Ar), 6.80 (dd, J = 8.7, 2.8 Hz, 2H, $H^{4,4'}$ of Ar), 3.90 (t, J = 6.6 Hz, 4H, OCH_2), 3.81 (t, J = 6.5 Hz, 4H, OCH_2), 1.78–1.70 (m, 4H, CH_2), 1.49–1.17 (m, 40H, CH_2), 0.91–0.84 (m, 12H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 152.8 (s, $C^{5,5'}$ of Ar), 150.7 (s, $C^{2,2'}$ of Ar), 129.3 (s, $C^{1,1'}$ of Ar), 117.7 (s, $C^{3,3'}$ of Ar), 114.3 (s, $C^{4,4'}$ and $C^{6,6'}$ of Ar), 69.7, 68.6 (each s, OCH_2), 31.8, 31.8, 29.4, 29.4, 29.4, 29.3, 29.3, 26.1, 26.0, 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd. for $C_{44}H_{74}O_4$: C, 79.22; H, 11.18. Found: C, 79.61; H, 11.28.

Synthesis of (*E*,*E*)-Bis(2-bromoethenyl)arenes (1, 10, 12 and 13). These compounds were prepared by a two-step procedure.



(i) (*E*,*E*)-Bis[2-(dimethylphenylsilyl)ethenyl]arene (21a–d).[13] A typical procedure is reported for (*E*,*E*)-**21a**. To a solution of $HSiMe_2Ph$ (1.9 mL, 12 mmol) and 1,4-diethynylbenzene (**20a**; 316 mg, 2.50 mmol) in CH_2Cl_2 (10 mL) was added $[RuHCl(CO)(PPh_3)_3]$ (238 mg, 0.250 mmol). The mixture was stirred for 2 h at room temperature, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexane and then hexane/CH_2Cl_2 (9/1)), and (*E*,*E*)-**21a** ((*E*,*E*) > 99/1) was isolated as a white solid (877 mg, 88% yield). Similarly, compounds (*E*,*E*)-**21b**, **21c**, and **21d** were synthesized from the corresponding diethenylarene (**20b–d**) in 95, 96, and 85% yields, respectively.

(*E*,*E*)-21a. White solid. Mp: 93–94 °C. ^{1}H NMR ($CDCl_3$): δ 7.60–7.54 (m, 4H, *m*-Ph), 7.40 (s, 4H, Ar), 7.39–7.34 (m, 6H, *o*- and *p*-Ph), 6.71 (d, J = 19.1 Hz, 2H, ArCH=), 6.58 (d, J = 19.1 Hz, 2H, =CHSi), 0.43 (s, 12H, $Si(CH_3)_2$). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 144.8 (s, ArCH=), 138.5 (s, *ipso*-C of Ph), 138.0 (s, $C^{1,4}$ of Ar), 133.9 (s, *o*-C of Ph), 129.1 (s, *p*-C of Ph), 127.8 (s, *m*-C of Ph), 127.3 (s, =CHSi), 126.7 (s, $C^{2,3,5,6}$ of Ar), –2.5 (s, $Si(CH_3)_2$). Anal. Calcd. for $C_{26}H_{30}Si_2$: C, 78.33; H, 7.58. Found: C, 78.31; H, 7.59.

(*E*,*E*)-21b. Purified by flash column chromatography (SiO_2, hexane). Colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.60–7.54 (m, 4H, *m*-Ph), 7.53 (s, 1H, H^2 of Ar), 7.39–7.32 (m, 8H, *o*- and *p*-Ph and $H^{4,6}$ of Ar), 7.28 (dd, J = 8.7, 6.2 Hz, 1H, H^5 of Ar), 6.93 (d, J = 19.1 Hz, 2H, ArCH=), 6.60 (d, J = 19.1 Hz, 2H, =CHSi), 0.43 (s, 12H, $Si(CH_3)_2$). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 145.1 (s, ArCH=), 142.3 (s, C^1 of Ph), 138.5, 138.4 (each s, *ipso*-C of Ph and $C^{1,3}$ of Ar), 133.9 (s, *o*-C of Ph), 129.1 (s, *p*-C of Ph), 128.7 (s, C^5 of Ar), 127.8 (s, *m*-C of Ph), 127.5 (s, =CHSi), 126.3 (s, $C^{4,6}$ of Ar), 124.6 (s, C^2 of Ar), –2.5 (s, $Si(CH_3)_2$). Anal. Calcd. for $C_{26}H_{30}Si_2$: C, 78.33; H, 7.58. Found: C, 78.48; H, 7.59.

(*E*,*E*)-21c. Purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2 (9/1)). White solid. Mp: 121–123 °C. ^{1}H NMR ($CDCl_3$): δ 7.61–7.54 (m, 4H, *m*-Ph), 7.58, 7.51 (each d, J = 8.3 Hz, 4H, C_6H_4), 7.40–7.34 (m, 6H, *o*- and *p*-Ph), 6.97 (d, J = 19.1 Hz, 2H, C_6H_4CH=), 6.62 (d, J = 19.1 Hz, 2H, =CHSi), 0.45 (s, 12H, $Si(CH_3)_2$). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 144.7 (s, C_6H_4CH=), 140.3 (s, C^1 of C_6H_4), 138.5 (s, *ipso*-C of Ph), 137.3 (C^4 of

C_6H_4), 133.9 (s, *o*-C of Ph), 129.1 (s, *p*-C of Ph), 127.8 (s, *m*-C of Ph), 127.4 (s, =CHSi), 127.0, 127.0 (each s, $C^{2,6}$ and $C^{3,5}$ of C_6H_4), –2.5 (s, $Si(CH_3)_2$). Anal. Calcd. for $C_{32}H_{34}Si_2$: C, 80.95; H, 7.22. Found: C, 80.98; H, 7.18.

(*E*,*E*)-21d. Purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2 (9/1)). White solid. Mp: 106–108 °C. ^{1}H NMR ($CDCl_3$): δ 7.70 (d, J = 7.9 Hz, 2H, $H^{4,5}$ of Fl), 7.63 (br s, 2H, $H^{1,8}$ of Fl), 7.62–7.57 (m, 4H, *m*-Ph), 7.44 (d, J = 7.9 Hz, 2H, $H^{3,6}$ of Fl), 7.40–7.36 (m, 6H, *o*- and *p*-Ph), 7.01 (d, J = 19.1 Hz, 2H, FlCH=), 6.62 (d, J = 19.1 Hz, 2H, =CHSi), 3.86 (s, 2H, CH_2), 0.45 (s, 12H, $Si(CH_3)_2$). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 145.5 (s, FlCH=), 144.0, 141.5 (each s, Fl), 138.7 (s, *ipso*-C of Ph), 137.0 (s, Fl), 133.9 (s, *o*-C of Ph), 129.0 (s, *p*-C of Ph), 127.8 (s, *m*-C of Ph), 126.5 (s, =CHSi), 125.9, 122.8, 120.0 (each s, Fl), 36.7 (s, CH_2), –2.5 (s, $Si(CH_3)_2$). Anal. Calcd. for $C_{33}H_{34}Si_2$: C, 81.42; H, 7.04. Found: C, 81.53; H, 7.12.

(ii) (*E*,*E*)-Bis(2-bromoethenyl)arene (1, 10, 12 and 13).[29] A typical procedure is reported for (*E*,*E*)-**1** (Ar = *p*-phenylene). To a solution of (*E*,*E*)-**21a** (598 mg, 1.50 mmol) in CH_3CN (60 mL) was added *N*-bromosuccinimide (1.07 g, 6.00 mmol) at room temperature, and the mixture was stirred for 3 h. 10% aqueous $Na_2S_2O_3$ solution (100 mL) was added, and the mixture was extracted with $CHCl_3$ (4 × 75 mL). The combined extracts were washed with 1 N aqueous NaOH (2 × 100 mL) and brine (100 mL), dried over $MgSO_4$, concentrated under reduced pressure. The crude product was recrystallized from Et_2O/MeOH at –30 °C to give (*E*,*E*)-**1** (>99% purity) as a white solid (311 mg, 72% yield). Similarly, (*E*,*E*)-**10** (Ar = *m*-phenylene), **12** (Ar = 4,4'-biphenylene), and **13** (Ar = 2,7-fluorenylene) were synthesized from (*E*,*E*)-**21b**–**d** in 56, 96, and 88% yields, respectively.

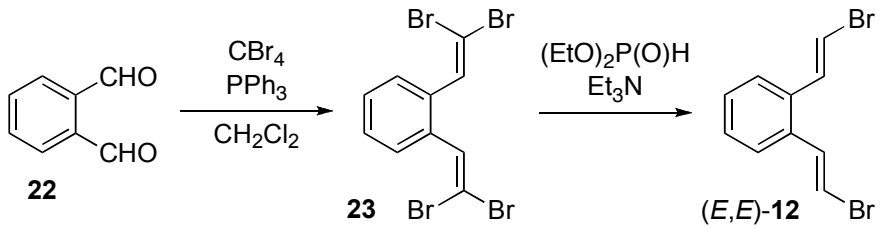
(*E*,*E*)-1. White solid. Mp: 139–141 °C. ^{1}H NMR ($CDCl_3$): δ 7.25 (s, 4H, Ar), 7.07 (d, J = 14.0 Hz, 2H, ArCH=), 6.79 (d, J = 14.0 Hz, 2H, =CHBr). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 136.6 (s, ArCH=), 135.7 (s, $C^{1,4}$ of Ar), 126.5 (s, $C^{2,3,5,6}$ of Ar), 107.1 (s, =CHBr). MS, *m*/*z* (relative intensity, %): 291 (M^+ + 3, 5), 290 (M^+ + 2, 42), 289 (M^+ + 1, 10), 288 (M^+, 88), 286 (M^+ – 1, 46), 209 (31), 207 (32), 129 (10), 128 (100), 127 (43), 126 (17), 103 (10), 102 (27), 101 (16), 77 (21), 76 (17), 75 (24), 74 (15), 64 (22), 63 (42), 52 (10), 51 (39), 50 (20). Anal. Calcd. for $C_{10}H_8Br_2$: C, 41.71; H, 2.80. Found: C, 41.63; H, 2.88.

(*E*,*E*)-10. Recrystallized from Et_2O/MeOH at –70 °C. White solid. Mp: 45 °C. ^1H NMR ($CDCl_3$): δ 7.29 (dd, J = 8.6, 6.5 Hz, 1H, H^5 of Ar), 7.23 (s, 1H, H^2 of Ar), 7.21 (d, J = 7.6 Hz, 2H, $H^{4,6}$ of Ar), 7.08 (d, J = 14.0 Hz, 2H, ArCH=), 6.79 (d, J = 14.0 Hz, 2H, =CHBr). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 136.6 (s, ArCH=), 136.5 (s, $C^{1,3}$ of Ar), 129.3 (s, C^5 of Ar), 125.8 (s, $C^{4,6}$ of Ar), 123.9 (s, C^2 of Ar), 107.4 (s, =CHBr). MS, *m*/*z* (relative intensity, %): 291 (M^+ + 3, 5), 290 (M^+ + 2, 40), 289 (M^+ + 1, 10), 288 (M^+, 87), 286 (M^+ – 1, 42), 209 (19), 207 (20), 129 (12), 128 (100), 127 (29), 126 (12), 104 (17), 103 (14), 102 (25), 101 (13), 77 (21), 76 (19), 75 (26), 74 (17), 64 (48), 63 (71), 62 (10), 52 (10), 51 (80), 50 (40). Anal. Calcd. for $C_{10}H_8Br_2$: C, 41.71; H, 2.80. Found: C, 41.79; H, 2.74.

(*E*,*E*)-11. Recrystallized from THF/MeOH at –30 °C. White solid. Mp: 217–219 °C. ^1H NMR ($CDCl_3$): δ 7.56, 7.37 (each d, J = 8.3 Hz, 4H, C_6H_4), 7.14 (d, J = 14.0 Hz, 2H, C_6H_4CH=), 6.82 (d, J = 14.0 Hz, 2H, =CHBr). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 140.2 (s, C^1 of C_6H_4), 136.7 (s, C_6H_4CH=), 135.1 (C^4 of C_6H_4), 127.2, 126.6 (each s, $C^{2,6}$ and $C^{3,5}$ of C_6H_4), 106.8 (s, =CHBr). MS, *m*/*z* (relative intensity, %): 367 (M^+ + 3, 8), 366 (M^+ + 2, 52), 365 (M^+ + 1, 18), 364 (M^+, 100), 363 (M^+ – 1, 9), 362(M^+ – 2, 52), 285 (11), 283 (11), 204 (20), 203 (28), 202 (55), 176 (15), 151 (10), 102 (42), 101 (44), 100 (12), 89 (20), 88 (27), 76 (25), 75 (15), 63 (10). Anal. Calcd. for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32. Found: C, 52.98; H, 2.20.

(*E*,*E*)-13. Recrystallized from CH_2Cl_2/MeOH at –30 °C. White solid. Mp: 204–206 °C. ^1H NMR ($CDCl_3$): δ 7.70 (d, J = 7.9 Hz, 2H, $H^{4,5}$ of Fl), 7.48 (br s, 2H, $H^{1,8}$ of Fl), 7.32 (d, J = 7.9 Hz, 2H, $H^{3,6}$ of Fl), 7.17 (d, J = 14.0 Hz, 2H, FlCH=), 6.82 (d, J = 14.0 Hz, 2H, =CHBr), 3.90 (s, 2H, CH_2). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 144.1, 141.4 (each s, Fl), 137.4 (s, FlCH=), 134.7, 125.4, 122.6, 120.3 (each s, Fl), 106.0 (s, =CHBr), 36.7 (s, CH_2). MS, *m*/*z* (relative intensity, %): 379 (M^+ + 3, 8), 378 (M^+ + 2, 45), 377 (M^+ + 1, 18), 376 (M^+, 88), 375 (M^+ – 1, 10), 374 (M^+ – 2, 46), 297 (13), 295 (18), 217 (15), 216 (79), 215 (100), 214 (15), 213 (32), 190 (13), 189 (49), 188 (17), 187 (19), 163 (10), 149 (14), 108 (32), 107 (78), 106 (13), 95 (32), 95 (70), 94 (12), 82 (16). Anal. Calcd. for $C_{17}H_{12}Br_2$: C, 54.29; H, 3.22. Found: C, 54.26; H, 3.24.

Synthesis of (*E*,*E*)-Bis-1,2-(2-bromoethenyl)benzene (12).



This compound was prepared by a two-step procedure.[30] (i) A solution of CBr_4 (14.6 g, 44.0 mmol) in CH_2Cl_2 (44 mL) was added dropwise to a solution of *o*-phthalaldehyde (**22**; 2.68 g, 20.0 mmol) and PPh_3 (22.0 g, 84.0 mmol) in CH_2Cl_2 (100 mL) at 0 °C. The mixture was stirred for 3 h at 0 °C, purified by column chromatography (SiO_2, hexane), giving bis-1,2-(2,2-dibromoethenyl)benzene (**23**) as an orange oil (8.04 g, 90% yield). The NMR data were identical to those reported.[31] ^{1}H NMR ($CDCl_3$): δ 7.53–7.49 (m, 2H, $H^{3,6}$ of Ar), 7.42 (s, 2H, CH=CBr_2), 7.40–7.35 (m, 2H, $H^{4,5}$ of Ar).

(ii) A mixture of **23** (4.46 g, 10.0 mmol), diethyl phosphite (9.0 mL, 70 mmol), and Et_3N (14 mL, 100 mmol) was stirred under reflux for 5 h. The reaction mixture was cooled to room temperature, poured into 1 N aqueous HCl (100 mL), and extracted with CH_2Cl_2 (4 × 50 mL). The combined extracts were washed with brine (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The resulting solid was purified by flash column chromatography (SiO_2, hexane) and then by recrystallization from CH_2Cl_2/hexane at –30 °C, giving colorless crystals of (*E*,*E*)-**12** (1.59 g, 55% yield). Mp: 66–68 °C. ^{1}H NMR ($CDCl_3$): δ 7.33–7.26 (m, 4H, Ar), 7.31 (d, *J* = 13.8 Hz, 2H, ArCH=), 6.67 (d, *J* = 13.8 Hz, 2H, =CHBr). ^{13}C{^{1}H}NMR ($CDCl_3$): δ 134.9 (s, ArCH=), 133.9 (s, $C^{1,2}$ of Ar), 128.6, 127.0 (each s, $C^{3,6}$ and $C^{4,5}$ of Ar), 109.0 (s, =CHBr). MS, *m*/*z* (relative intensity, %): 288 (M^+, 1), 209 (4), 207 (4), 129 (11), 128 (100), 127 (10), 126 (4), 102 (5), 77 (5), 76 (3), 75 (5), 64 (6), 63 (10), 51 (8), 50 (4). Anal. Calcd. for $C_{10}H_8Br_2$: C, 41.71; H, 2.80. Found: C, 42.00; H, 2.79.

Synthesis of All-trans PpPV (3). A 10 mL Schlenk tube was charged with (*E*,*E*)-**1** (57.6 mg, 0.200 mmol), **2a** (84.4 mg, 0.200 mmol), Bu_4NBr (64.5 mg, 0.200 mmol), toluene

(2 mL) and 3.0 M aqueous NaOH (0.20 mL, 0.60 mmol). [Pd(PBu^t_3)$_2$] (1.5 mg, 3.0 μmol) was added, and the mixture was stirred at 80 °C for 24 h. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (5 mL), washed with water, and then poured into a vigorously stirred MeOH (50 mL). An orange precipitate of all-trans **3** was collected by membrane filter (0.5 μm), washed with MeOH, and dried under vacuum at room temperature overnight (94.4 mg, >99% yield). ^{1}H NMR ($CDCl_3$): δ 7.53 (s, C_6H_4), 7.50 (d, *J* = 16.5 Hz, CH=CH), 7.50–7.45 (m, $H^{2,6}$ of terminal C_6H_4CH=CHBr), 7.30 (d, *J* = 8.6 Hz, $H^{3,5}$ of terminal C_6H_4CH=CHBr), 7.15 (d, *J* = 16.7 Hz, CH=CH), 7.14 (s, $H^{3,6}$ of C_6H_2), 7.11 (d, *J* = 14.2 Hz, C*H*=CHBr of terminal C_6H_4CH=CHBr), 6.83 (d, *J* = 9.1 Hz, H^3 of terminal $C_6H_3(OC_8H_{17})_2$), 6.79 (d, *J* = 14.0 Hz, 1H, CH=C*H*Br), 6.77 (dd, *J* = 8.9, 2.8 Hz, H^4 of terminal $C_6H_3(OC_8H_{17})_2$), 4.08 (t, *J* = 6.0 Hz, OCH_2), 3.98 and 3.96 (t, *J* = 6.3 Hz, OCH_2 of terminal $C_6H_3(OC_8H_{17})_2$), 1.96–1.80 and 1.62–1.18 (m, CH_2), 0.94–0.80 (m, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.2 (s, $C^{2,5}$ of C_6H_2), 137.2 (s, $C^{1,4}$ of C_6H_4), 128.5 (s, CH=CH), 127.0 (s, $C^{1,2}$ of C_6H_2), 126.8 (s, $C^{2,3,5,6}$ of C_6H_4), 123.2 (s, CH=CH), 110.6 (s, $C^{3,6}$ of C_6H_2), 69.6 (s, OCH_2), 31.8, 29.5, 29.4, 29.3, 26.3, 22.7 (each s, CH_2), 14.1 (s, CH_3).

Synthesis of All-trans PAVs (14–17). These polymers were synthesized similarly to all-trans PpPV (**3**) using (*E*,*E*)-**10**–**13** (0.200 mmol), **2b** (117 mg, 0.200 mmol), THF (2 mL), 3.0 M aqueous NaOH (0.20 mL, 0.60 mmol), and [Pd(PBu^t_3)$_2$] (1.5 mg, 3.0 μmol) at room temperature for 24 h.

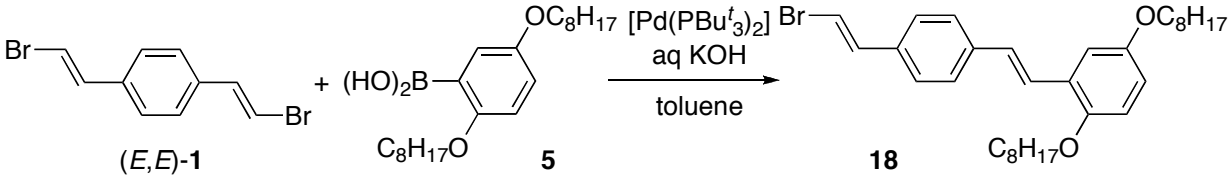
All-trans 14. Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.65 (s, H^2 of C_6H_4), 7.54 (d, *J* = 16.3 Hz, CH=CH), 7.48 (d, *J* = 7.5 Hz, $H^{4,6}$ of C_6H_4), 7.38 (t, *J* = 7.3 Hz, H^5 of C_6H_4), 7.22–7.13 (m, $H^{3,6}$ of C_6H_2 and CH=CH), 4.10 (t, *J* = 6.0 Hz, OCH_2), 1.96–1.83 and 1.63–1.18 (m, CH_2), 0.92–0.80 (m, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.2 (s, $C^{2,5}$ of C_6H_2), 138.3 (s, $C^{1,3}$ of C_6H_4), 128.9 (s, CH=CH), 127.0 (s, $C^{1,2}$ of C_6H_2), 125.5, 125.3 (each s, C^2 and C^6 of C_6H_4), 123.8 (s, CH=CH), 110.9 (s, $C^{3,6}$ of C_6H_2), 69.7 (s, OCH_2), 31.8, 29.5, 29.4, 29.4, 26.3, 22.7 (each s, CH_2), 14.1 (s, CH_3).

All-trans 15. Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.70–7.58 (m, C_6H_4), 7.53 (d, J = 16.2 Hz, CH=CH), 7.37 (d, J = 16.2 Hz, CH=CH), 7.32–7.22 (m, C_6H_4), 7.12 (s, $H^{3,6}$ of C_6H_2), 3.99 (t, J = 6.3 Hz, OCH_2), 1.83–1.68 and 1.50–1.12 (m, CH_2), 0.90–0.77 (m, CH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 151.2 (s, $C^{2,5}$ of C_6H_2), 136.7 (s, $C^{1,2}$ of C_6H_4), 127.5 (s, CH=CH), 127.2 (s, $C^{1,4}$ of C_6H_2), 126.9, 126.8, 126.1 (each s, $C^{3,6}$ and $C^{4,5}$ of C_6H_4 and CH=CH), 110.8 (s, $C^{3,6}$ of C_6H_2), 69.5 (s, OCH_2), 31.8, 29.5, 29.4, 29.4, 26.3, 22.7 (each s, CH_2), 14.1 (s, CH_3).

All-trans 16. Yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.70–7.48 (m, C_6H_4), 7.55 (d, J = 16.3 Hz, CH=CH), 7.19 (d, J = 16.3 Hz, CH=CH), 7.17 (s, $H^{3,6}$ of C_6H_2), 4.09 (t, J = 6.3 Hz, OCH_2), 1.96–1.80 and 1.63–1.18 (m, CH_2), 0.94–0.82 (m, CH_3). $^{13}C\{^{1}H\}$ NMR analysis was not feasible due to low solubility.

All-trans 17. Orange solid. ^{1}H NMR ($CDCl_3$): δ 7.83–7.68 and 7.62–7.46 (m, Fl), 7.55 (d, J = 16.0 Hz, CH=CH), 7.24–7.10 (m, $H^{3,6}$ of C_6H_2 and CH=CH), 4.10 (t, J = 6.3 Hz, OCH_2), 1.97–1.81 and 1.65–1.18 (m, CH_2), 0.96–0.82 (m, CH_3). $^{13}C\{^{1}H\}$ NMR analysis was not feasible due to low solubility.

Synthesis of (*E*,*E*)-2,5-Dioctyloxy-4'-(2-bromoethenyl)stilbene (18).



To a solution of (*E*,*E*)-**1** (130 mg, 0.450 mmol) and **5** (114 mg, 0.300 mmol) in toluene (1.5 mL) were successively added $[Pd(PBu^{t}_3)_2]$ (2.3 mg, 4.5 μmol) and 3.0 M aqueous KOH (0.30 mL, 0.90 mmol). The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was passed through a short column (SiO_2, hexane/CH_2Cl_2 (1/1)), and purified by flash column chromatography (SiO_2, hexane and then hexane/CH_2Cl_2 (10/1)), giving the title compound as a yellow solid (89.2 mg, 55% yield). Mp: 44–46 °C. ^{1}H NMR ($CDCl_3$): δ 7.47 (d, J = 16.3 Hz, 1H, C_6H_3CH=CH), 7.46 (d, J = 8.3 Hz, 2H, $H^{2',6'}$ of C_6H_4), 7.28 (d, J = 8.2 Hz, 2H, $H^{3',5'}$ of C_6H_4), 7.13 (d, J = 3.7 Hz, 1H, H^{6} of C_6H_3), 7.10 (d, J = 14.0

Hz, 1H, C*H*=CHBr), 7.07 (d, *J* = 16.5 Hz, 1H, C_6H_3CH=C*H*), 6.83 (d, *J* = 8.9 Hz, 1H, H^3 of C_6H_3), 6.78 (d, *J* = 13.9 Hz, 1H, CH=C*H*Br), 6.78 (dd, *J* = 9.1, 2.8 Hz, 1H, H^4 of C_6H_3), 3.96 (t, *J* = 6.3 Hz, 2H, OCH_2), 3.95 (t, *J* = 6.4 Hz, 2H, OCH_2), 1.87–1.73 (m, 4H, CH_2), 1.54–1.23 (m, 20H, CH_2), 0.93–0.85 (m, 6H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 153.3, 151.0 (each s, $C^{2,5}$ of C_6H_3), 138.0, 134.8 (each s, $C^{1',4'}$ of C_6H_4), 136.9 (s, *C*H=CHBr), 128.3 (s, CH=CH), 127.3 (s, C^1 of C_6H_3), 126.9, 126.4 (each s, $C^{2',3',5',6'}$ of C_6H_4), 124.1 (s, CH=CH), 114.7, 113.9, 112.3 (each s, $C^{3,4,6}$ of C_6H_3), 106.2 (s, CH=*C*HBr), 69.5, 68.7 (each s, OCH_2), 31.8, 31.8, 29.5, 29.4, 29.4, 29.3, 29.3, 26.3, 26.3, 26.1, 22.7 (each s, CH_2), 14.1 (s, CH_3). Anal. Calcd. for $C_{32}H_{45}BrO_2$: C, 70.96; H, 8.37. Found: C, 70.81; H, 8.45.

Photo-induced Insolubilization of PpPV. A solution of PpPV in $CHCl_3$ (2.0 wt%) was passed through a syringe filter (DISMIC-13 JP, PTFE 0.50 μm, Hydrophobic; ADVANTEC). A thin film of PpPV was prepared by spin coating on a quartz plate (1 cm^2); the filtrate (50 μL) was added dropwise on a plate, and the plate was accelerated to 1200 rpm for 2 s, kept at this rate for 10 s, and then rotated at 2000 rpm for 60 s. After drying under vacuum at room temperature for 30 min, the film was placed in a quartz cell under N_2 atmosphere, and then analyzed by UV–vis absorption spectroscopy. Next, the film was placed in a stainless-steel holder with a quartz window, and irradiated by a Xe lamp (λ_{max} = 365 nm, 21.0 mW cm^{-2}) for 60 min under vacuum at room temperature. UV-vis absorption spectrum of the resulting film was then recorded. The film was rinsed twice in $CHCl_3$ (each 3 mL) with light shaking, dried under vacuum at room temperature, and examined by UV-vis absorption spectroscopy.

Measurement of Carrier Mobility. All manipulations were carried out in an argon-filled glove box. An OFET device was fabricated in a top-contact configuration on a *p*-type Si wafer as a gate electrode (one-side polished, < 0.02 Ω resistance, Furuuchi Chemical Co.) with 3000-Å-thick SiO_2 (C_i = 11 nF cm^{-2}) as a dielectric film. A plate was cut and washed in 2-propanol under ultrasonic wave and under boiling. A thin film of PpPVs as

the active layer (ca. 30 nm thick) was deposited on the Si/SiO_2 substrate by spin-coating a 0.1–0.5 wt% solution in $CHCl_3$ at 100–8000 rpm for 60 s, and dried under vacuum at room temperature, and irradiated by a Xe lamp (λ_{max} = 365 nm, 23.0 mW cm^{-2}) for 1 h. On the top of the thin film, gold films (30 nm) as source and drain electrodes were deposited through a mask. A drain-source channel length (L) and width (W) were 20 μm and 5 mm, respectively. Characteristics of OFET devices were evaluated at room temperature with two source meters (2400, Keithley Instruments Inc.). Carrier mobility (μ_{FET}) was calculated in the saturation regime (V_d = 100 V) of the I_d using the following equation,

$$I_d = (WC_i/2L)\ \mu_{FET}\ (V_g - V_t)^2$$

where C_i is the capacitance of the SiO_2 insulator, and V_g and V_t are the gate and threshold voltages, respectively. In another case, the PPV thin film was rinsed twice with toluene (1 mL) after UV-irradiation, and examined in a similar manner.

References and notes

(1) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539–541. (b) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47–49. (c) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628–630. (d) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477–479. (e) Welter, S.; Brunner, K.; Hofstraat, J. W.; De Cola, L. *Nature* **2003**, *421*, 54–57.

(2) (a) A. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402–428. (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121–128. (c) Scherf, U. *Top. Curr. Chem.* **1999**, *201*, 163–222. (d) Akcelrud, L. *Prog. Polym. Sci.* **2003**, *28*, 875–962.

(3) (a) Tessler, N.; Denton, G. J.; Friend, R. H. *Nature* **1996**, *382*, 695–697. (b) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Andersson, M. R.; Pei, Q.; Heeger, A. J. *Science* **1996**, *273*, 1833–1836. (c) McGehee, M. D.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 1655–1668. (d) Nguyen, T.-Q.; Martini, I. B.; Liu, J.; Schwartz, B. J. *J. Phys. Chem. B* **2000**, *104*, 237–255.

(4) (a) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789–1791. (b) Dittmer, J. J.; Petritsch, K.; Marseglia, E. A.; Friend, R. H.; Rost, H.; Holmes, A. B. *Synth. Met.* **1999**, *102*, 879–880. (c) Gebeyehu, D.; Brabec, C. J.; Padinger, F.; Fromherz, T.; Hummelen, J. C.; Badt, D.; Schindler, H.; Sariciftci, N. S. *Synth. Met.* **2001**, *118*, 1–9. (d) Martens, T.; D'Haen, J.; Munters, T.; Beelen, Z.; Goris, L.; Manca, J.; D'Olieslaeger, M.; Vanderzande, D.; De Schepper, L.; Andriessen, R. *Synth. Met.* **2003**, *138*, 243–247.

(5) (a) Gailberger, M.; Baessler, H. *Phys. Rev. B* **1991**, *44*, 8643–8651. (b) Kryukov, A. Yu.; Saidov, A. Ch.; Vannikov, A. V. *Thin Solid Films* **1992**, *209*, 84–91. (c) Meyer, H.; Haarer, D.; Naarmann, H.; Hoerhold, H. H. *Phys. Rev. B* **1995**, *52*, 2587–2598. (d) Pichler, K.; Jarrett, C. P.; Friend, R. H.; Ratier, B.; Moliton, A. *J. Appl. Phys.* **1995**, *77*, 3523–3527. (e) Blom, P. W. M.; de Jong, M. J. M.; Vleggaar, J. J. M. *Appl. Phys. Lett.* **1996**, *68*, 3308–3310. (f) Hoofman, R. J. O. M.; De Haas, M.; Siebbeles, L. D. A.; Warman, J. M. *Nature* **1998**, *392*, 54–56. (g) Geens, W.; Shaheen, S. E.; Wessling, B.; Brabec, C. J.; Poortmans, J.; Serdar Sariciftci, N. *Org. Electron.* **2002**, *3*, 105–110. (h) Roichman, Y.; Tessler, N. *Appl. Phys. Lett.* **2002**, *80*, 151–153. (i) Tzeng, K. L.; Meng, H. F.; Tzeng, M. F.; Chen, Y. S.; Liu, C. H.; Horng, S. F.; Yang, Y. Z.; Chang, S. M.; Hsu, C. S.; Chi, C. C. *Appl. Phys. Lett.* **2004**, *84*, 619–621. (j) Muratsubaki, M.; Furukawa, Y.; Noguchi, T.; Ohnishi, T.; Fujiwara, E.; Tada, H. *Chem. Lett.* **2004**, *33*, 1480–1481. (k) Chua, L.-L.; Zaumseil, J.; Chang, J.-F.; Ou, E. C.-W.; Ho, P. K.-H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194–199. (l) van Breemen, A. J. J. M.; Herwig, P. T.; Chlon, C. H. T.; Sweelssen, J.; Schoo, H. F. M.; Benito, E. M.; de Leeuw, D. M.; Tanase, C.; Wildeman, J.; Blom, P. W. M. *Adv. Funct. Mater.* **2005**, *15*, 872–876.

(m) Tanase, C.; Wildeman, J.; Blom, P. W. M. *Adv. Funct. Mater.* **2005**, *15*, 2011–2015. (n) Tanase, C.; Wildeman, J.; Blom, P. W. M.; Mena Benito, M. E.; de Leeuw, D. M.; van Breemen, A. J. J. M.; Herwig, P. T.; Chlon, C. H. T.; Sweelssen, J.; Schoo, H. F. M. *J. Appl. Phys.* **2005**, *97*, 123703/1–123703/6. (o) Todescato, F.; Capelli, R.; Dinelli, F.; Murgia, M.; Camaioni, N.; Yang, M.; Bozio, R.; Muccini, M. *J. Phys. Chem. B* **2008**, *112*, 10130–10136.

(6) (a) Wessling, R. A.; Zimmerman, R. G. U.S. Patent No 3401152, **1968**. (b) Lenz, R. W.; Han, C. C.; Stenger-Smith, J.; Karasz, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 3241–3249. (c) Batten, J. H.; Duran, R. S. *Macromolecules* **1998**, *31*, 3148–3150.

(7) (a) Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci., Part A-1: Polym. Chem.* **1966**, *4*, 1337–1349. (b) Baigent, D. R.; Greenham, N. C.; Gruener, J.; Marks, R. N.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. Hsieh, B. R.; Yu, Y.; VanLaeken, A. C.; Lee, H. *Macromolecules* **1997**, *30*, 8094–8095. (c) Schwalm, T.; Wiesecke, J.; Immel, S.; Rehahn, M. *Macromolecules* **2007**, *40*, 8842–8854.

(8) (a) Wadsworth, W. S. *Org. React.* **1977**, *25*, 73–253. (b) Ahn, T.; Jang, M. S.; Shim, H.-K.; Hwang, D.-H.; Zyung, T. *Macromolecules* **1999**, *32*, 3279–3285.

(9) (a) Thorn-Csányi, E.; Pflug, K. P. *J. Mol. Catal.* **1992**, *76*, 101–105. (b) Bazan, G. C.; Miao, Y.-J.; Renak, M. L.; Sun, B. J. *J. Am. Chem. Soc.* **1996**, *118*, 2618–2624. (c) Wagaman, M. W.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3978–3985. (d) Yu, C.-Y.; Turner, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7797–7800.

(10) (a) Thorn-Csányi, E.; Pflug, K. P. *J. Mol. Catal.* **1994**, *90*, 69–74. (b) Schlick, H.; Stelzer, F.; Tasch, S.; Leising, G. *J. Mol. Catal. A: Chem.* **2000**, *160*, 71–84. (c) Nomura, K.; Miyamoto, Y.; Morimoto, H.; Geerts, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6166–6177.

(11) (a) Greiner, A.; Heitz, W. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 581–588. (b) Suzuki, M.; Lim, J. C.; Saegusa, T. *Macromolecules* **1990**, *23*, 1574–1579. (c) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281–5286.

(12) (a) Babudri, F.; Cicco, S. R.; Farinola, G. M.; Naso, F.; Bolognesi, A.; Porzio, W. *Macromol. Rapid Commun.* **1996**, *17*, 905–911. (b) Babudri, F.; Cicco, S. R.; Chiavarone, L.; Farinola, G. M.; Lopez, L. C.; Naso, F.; Scamarcio, G. *J. Mater. Chem.* **2000**, *10*, 1573–1579. (c) Babudri, F.; Cardone, A.; Chiavarone, L.; Ciccarella, G.; Farinola, G. M.; Naso, F.; Scamarcio, G. *Chem. Commun.* **2001**, 1940–1941.

(13) Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet. Chem.* **2003**, *676*, 49–54.

(14) Prukala, W.; Pawluc, P.; Posala, K.; Marciniec, B. *Synlett* **2008**, 41–44.

(15) (a) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Umeda, K.; Akamatsu, K.; Tsuruoka, T.; Nawafune, H.; Ozawa, F. *J. Am. Chem. Soc.* **2005**, *127*, 4350–4353. (b) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Fukuse, Y.; Wakioka, M.; Ozawa, F. *Macromolecules* **2006**, *39*, 2039–2048.

(16) Miyanishi, S.; Tajima, K.; Hashimoto, K. *Macromolecules* **2009**, *42*, 1610–1618, and references therein.

(17) All-trans PpPV (M_n = 7200, M_w/M_n = 1.81), prepared by Hiyama-type polycondensation of 2,5-dioctyloxy-1,4-diiodobenzene with (*E*,*E*)-bis(2-silylethenyl)benzene,[13] scarcely remained on a quartz substrate (8%) after UV-irradiation (λ_{max} = 365 nm, 21.0 mW cm^{-2}) on a thin film for 1 h at room temperature, followed by rinsing twice with $CHCl_3$.

(18) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483. (b) Miyaura N. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A.; Diederich, F. Eds; WILEY-VCH, Weinheim, Germany, 2004; Chapter 2.

(19) A spin-coated film of all-trans **3** (M_n = 9700) on a quartz substrate was allowed to stand for 1 h at room temperature under vacuum in the dark. After rinsing the film twice with $CHCl_3$, 6% of PpPV remained on the substrate as confirmed by UV-vis absorption spectroscopy.

(20) Coulson, D. R. *Inorg. Synth.* **1971**, *13*, 121–124.

(21) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850–5858.

(22) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45–64.

(23) Dolby, L. J.; Wilkins, C.; Frey, T. G. *J. Org. Chem.* **1966**, *31*, 1110–1116.

(24) Johansson, D. M.; Wang, X.; Johansson, T.; Inganaes, O.; Yu, G.; Srdanov, G.; Andersson, M. R. *Macromolecules* **2002**, *35*, 4997–5003.

(25) Hu, Q.-S; Huang, W.-S.; Vitharana, D.; Zheng, X.-F.; Pu, L. *J. Am. Chem. Soc.* **1997**, *119*, 12454–12464.

(26) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627–630.

(27) Sumiya, K.; Kwak, G.; Sanda, F.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2774–2783.

(28) Katayama, H.; Nagao, M.; Ozawa, F.; Ikegami, M.; Arai, T. *J. Org. Chem.* **2006**, *71*, 2699–2705.

(29) Nagao, M.; Asano, K.; Umeda, K.; Katayama, H.; Ozawa, F. *J. Org. Chem.* **2005**, *70*, 10511–10514.

(30) Venkatesan, D.; Yoneda, M.; Ueda, M. *React. Funct. Polym.* **1996**, *30*, 341–352.

(31) Borst, M. L. G.; Bulo, R. E.; Winkel, C. W.; Gibney, D. J.; Ehlers, A. W.; Schakel, M.; Lutz, M.; Spek, A. L.; Lammertsma, K. *J. Am. Chem. Soc.* **2005**, *127*, 5800–5801.

List of Publications

General Introduction

"Structure-Controlled Synthesis of π-Conjugated Polymers by Means of Transition-Metal Catalysts"

Masayuki Wakioka, Ryo Takita, and Fumiyuki Ozawa

NIPPON GOMU KYOKAISHI **2008**, *81*, 431–437.

Chapter 1

"Effects of Primary Structures on Photo-induced Insolubilization of Poly(phenylenevinylene)s in Thin Films"

Yuichiro Mutoh, Yasutaka Yamamoto, Masayuki Wakioka, Ryo Takita, Jun-ichi Nakamura, Toshiya Iida, and Fumiyuki Ozawa

Chem. Asian. J., submitted for publication.

Chapter 2

"Stereocontrolled Synthesis and Photochemical Properties of All-cis and All-trans Poly(*m*-phenylenevinylene)s"

Masayuki Wakioka, Yasutaka Yamamoto, and Fumiyuki Ozawa

J. Polym. Sci., Part A: Polym. Chem., to be submitted.

Chapter 3

"Reaction of *trans*-Pd(styryl)Br($PMePh_2$)$_2$ with Styryl Bromide Affording 1,4-Diphenylbutadiene. An Unexpected Homo-Coupling Process Induced by P–C Reductive Elimination"

Masayuki Wakioka, Masato Nagao, and Fumiyuki Ozawa

Organometallics **2008**, *27*, 602–608.

Chapter 4

"Mechanism of C–P Reductive Elimination from *trans*-[Pd(CH=CHPh)Br($PMePh_2$)$_2$]"

Masayuki Wakioka, Yumiko Nakajima, and Fumiyuki Ozawa

Organometallics, **2009**, *28*, 2527–2534.

Chapter 5

"A Highly Selective Catalytic System for the Cross-Coupling of (*E*)-Styryl Bromide with Benzeneboronic Acid: Application to the Synthesis of All-trans Poly(arylenevinylene)s"

Masayuki Wakioka, Yuichiro Mutoh, Ryo Takita, and Fumiyuki Ozawa

Bull. Chem. Soc. Jpn., in press.

Other Publication

"Stereocontrolled Synthesis and Characterization of All-cis Poly(arylenevinylene)s"

Hiroyuki Katayama, Masato Nagao, Tatsuro Nishimura, Yukio Matsui, Yosuke Fukuse, Masayuki Wakioka, and Fumiyuki Ozawa

Macromolecules **2006**, *39*, 2039–2048.

"Possibility of Living Radical Polymerization of Vinyl Acetate Catalyzed by Iron(I) Complex"

Masayuki Wakioka, Kyung-Youl Baek, Tsuyoshi Ando, Masami Kamigaito, and Mitsuo Sawamoto

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Masayuki Wakioka

Department of Energy and Hydrocarbon Chemistry
Graduate School of Engineering
Kyoto University
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