# Unexpected Hydrodeiodo Sonogashira−Heck−Casser Coupling Reaction of 2,2′-Diiodobiphenyls with Acetylenes

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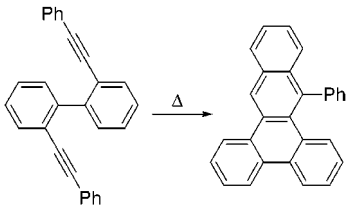
2,2′-Diiodobiphenyl-4,4′-dicarboxylic acid dimethyl ester (**3**) undergoes either a ring-closure reaction with phenylacetylene to give **4** or hydrodeiodo phenylethynylation to give **5** under the catalytic conditions of $Pd(OAc)_2$/CuI/phosphine in amines. In these reactions, the amine and the phosphine ligands play important roles in controlling the reactivity. Among the ligands we used, tris(*o*-tolyl)-phosphine is the best ligand for hydrodeiodo phenylethynylation, while the bidentate phosphine ligand retards both of the reactions. On the basis of our results, we propose that **5** is formed through a fast hydrodeiodination, followed by a Sonogashira phenylethynylation. The results of the deuterium labeling experiments show that proton exchange between the acetylenic proton and the alkyl protons of amine occurs effectively under the reaction conditions. In addition, the hydrogen that replaces the iodide in the hydrodeiodination process arises mainly from the acetylenic proton.

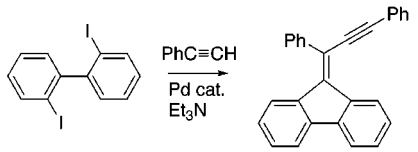


The Sonogashira−Heck−Cassar (SHC) palladium-catalyzed coupling reaction of aryl halides with terminal acetylenes has played an important role in internal acetylene synthesis.[1,2] Recently, we were interested in developing conjugated polymers based on novel polyaromatic compounds.[3] Thermal cyclization behavior of 2,2′-bis(phenylethynyl)biphenyl (**1**) intrigues us because it provides a useful synthetic tactic for polyaromatic compounds with highly fused nuclei.[4] According to the literature, **1** could be synthesized directly from 2,2′-diiodobiphenyl and cuprous phenylacetylide.[4]

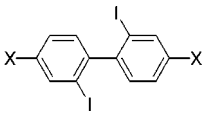



**1**

Although the SHC reaction has been widely used for aryl halide−acetylene coupling, a literature search reveals that the unexpected fluorenyl derivative **2**, instead of **1**, would be obtained under SHC conditions.[5] If 2,2′-dibromobiphenyl was employed, the incomplete phenylethynylation product would be obtained in low yield.[5a]




This unusual reaction behavior prompts us to revisit the SHC reaction of 2,2′-diiodobiphenyls. Because we are interested in the polymer applications of these materials, we have focused particular attention on the reaction behavior of the 4,4′-disubstituted derivative **3** in our study.




**3** X = $CO_2Me$

## Results and Discussion

Table 1 summarizes the reaction conditions we have used for the coupling of **3** in the presence of excess PhC≡CH. Under common SHC conditions, such as $Pd(OAc)_2$/CuI/$PPh_3$/$Et_3N$[1] or $Pd(OAc)_2$/TBABr/$K_2CO_3$/DMF,[6] Lau's fluorenyl derivative **4a** was isolated as the major product. However, if the reaction was carried out in the presence of $Pd(OAc)_2$/CuI/P(*o*-tolyl)$_3$/PhMe/$Et_2NH$,[7] monophenylethynylated derivative **5a** predominated. It is noteworthy to emphasize that this unusual symbiotic reaction behavior[8] leads one of the iodo group to hydrodeiodination and the other to the SHC alkynylation.Changing the

* Corresponding author.

(1) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467. (b) Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259. (c) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253.

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(3) For examples, see: (a) Lin, S.-C.; Chen, J. A.; Liu, M.-H.; Su, Y. O.; Leung, M.-k. *J. Org. Chem.* **1998**, *63*, 5059. (b) Mandal, A. B.; Lee, G.-H.; Liu, Y. H.; Peng, S.-M.; Leung, M.-k. *J. Org. Chem.* **2000**, *65*, 332.

(4) Kandil, S. A.; Dessy, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 3027.

(5) (a) Dougherty, T. K.; Lau, K. S. Y.; Hedberg, F. L. *J. Org. Chem.* **1983**, *48*, 5273. (b) König, B.; Bubenitschek, P.; Jones, P. G. *Liebigs Ann.* **1995**, 195.

(6) (a) Larock, R. C.; Yum, E. K. *Synlett* **1990**, 529. (b) Nguefack, J.-F.; Bolitt, V.; Sinou, D. *Tetrahedron Lett.* **1996**, *37*, 5527. (c) Okuro, K.; Furuune, M.; Enna, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1993**, *58*, 4716.

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**Table 1. Phenylethynylation of 3 Catalyzed by $Pd(OAc)_2$ under Various Conditions**

| reagents (temp/°C) | **4a** (%) | **5a** (%) | SM[a] (%) |
|---|---|---|---|
| CuI, $PPh_3$, $Et_3N$ (80) | 93 | 7 | |
| TBABr, $K_2CO_3$, DMF (100) | 62 | 4 | 34 |
| CuI, P(*o*-tolyl)$_3$, DMF, $Et_3N$ (70) | | 89 | 11 |
| CuI, P(*o*-tolyl)$_3$, PhMe, $Et_2NH$ (room) | 36 | 64 | |
| CuI, P(*o*-tolyl)$_3$, THF, $Et_2NH$ (room) | | 46 | 54 |
| CuI, P(*o*-tolyl)$_3$, $Et_2NH$ (room) | | 78 | 22 |
| CuI, P(*o*-tolyl)$_3$, $Et_2NH$ (60) | | 100 | |

[a] SM: recovery of the starting material.

**Table 2. Stoichiometry of the Hydrodeiodo Phenylethynylation of 3[a]**

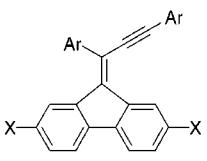
| $n$[d] | $P(Ar)_3$ | time (h) | product (%) | recovery (%) |
|---|---|---|---|---|
| 1 | $P(Ph)_3$ | 4 | 30 | 70 |
| 2 | P(*o*-tolyl)$_3$ | 4 | 83 | 17 |
| 2.5 | $P(Ph)_3$ | 2 | 100 (73)[b,c] | |
| 3 | P(*o*-tolyl)$_3$ | 2 | 100 (80)[b] | |

[a] Reagents used in these experiments: **3**, $Et_2NH$, CuI (5 mol %), $Pd(OAc)_2$, $P(Ar)_3$. [b] Isolated yield. [c] Diphenyldiacetylene was isolated in 70% yield. [d] $n$ = equiv of PhC≡CH used.

solvent from PhMe/$Et_2NH$ to either THF/$Et_2NH$[9] or $Et_2NH$[1,10] gave **5a** as the exclusive product. Another independent preliminary study reveals that similar reactions also occur with 4,4′-dinitro-2,2′-diiodobiphenyl, indicating the general reactivity of **3** toward 2,2′-diiodobiphenyls.

The stoichiometry of the reaction in $Et_2NH$ was evaluated, and the results are summarized in Table 2. After considerable experimentation, the stoichiometric ratio of **3** to PhC≡CH was found to be 1:3. Incomplete conversion of **3** to the product occurred if only 2 equiv of PhC≡CH was used. In addition, over 70% of the oxidatively coupled PhC≡C−C≡CPh was isolated from the reaction mixture, indicating that PhC≡CH acts as a reducing agent in the reduction of the iodo group. It has been proposed in the literature that PhC≡CH may be involved in the SHC catalytic cycle by converting Pd(II) back to Pd(0).[1a]

The substituent at the 4 position of phenylacetylene affects its reactivity in the hydrodeiodo SHC reaction. (Table 3) While the introduction of an electron-withdrawing group such as $-NO_2$ slows down the reaction, the introduction of an electron-donating alkoxy group increases the relative yield percentage of the corresponding fluorenyl derivative **4**.



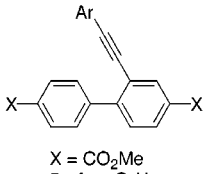




**Table 3. Substituent Effects on the Hydrodeiodo Phenylethynylation of 3[a]**

| R | time (h) | **4** (%) | **5** (%) | SM (%) |
|---|---|---|---|---|
| H | 2 | | **5a** (80) | |
| $OC_8H_{17}$ | 4 | **4b** (14) | **5b** (66) | |
| OMe | 4.5 | **4c** (14) | **5c** (60) | |
| $NO_2$ | 4 | | **5d** (63) | 37 |

[a] Reagents used in these reactions: $Pd(OAc)_2$, P(*o*-tolyl)$_3$, $Et_2NH$, CuI at 80 °C.

**Table 4. Solvent Effects on the Hydrodeiodo Phenylethynylation of 3[a]**

| amine | **4a** (%) | **5a** (%) | SM (%) | time (h) |
|---|---|---|---|---|
| $Et_2NH$ | | 100 | | 2 |
| $Et_3N$ | 5 | 53 | 42 | 2 |
| piperidine | | 100 | | 2.5 |
| pyrrolidine | | [b] | | 2.5 |
| *n*-$Bu_2NH$ | | 82 | 18 | 2 |
| *n*-$BuNH_2$ | | [b] | | 2.5 |
| $(TMS)_2NH$ | | | 100 | 24 |
| *i*-$Pr_2NH$ | 70 | 7 | 23 | 4 |
| *t*-$BuNH_2$ | 11 | 79 | | 2 |

[a] Reagents used in these reactions: $Pd(OAc)_2$, P(*o*-tolyl)$_3$, amine, CuI at 80 °C. [b] An unidentified mixture was obtained.

**Table 5. Ligand Effects on the Hydrodeiodo Phenylethynylation of 3[a]**

| | $Et_2NH$ | | $Et_3N$ | |
|---|---|---|---|---|
| ligand | **4a** (%)[c] | **5a** (%)[c] | **4a** (%)[c] | **5a** (%)[c] |
| $PPh_3$ (0.2 equiv) | | 73 | 81 | 5 |
| $PPh_3$ (1.1 equiv) | [b] | | | |
| dppf | | 9 | 45 | 20 |
| (*s*)-BINAP | | 15 | 27 | 25 |
| P(*o*-tolyl)$_3$ | | 80 | 5 | 53 |

[a] Reagents used in these reactions: $Pd(OAc)_2$, phosphine ligand, amine, CuI at 80 °C, 4 h. [b] No reaction. [c] Isolated yield.

Next, we turned our attention to the study of solvent effects (Table 4). Although the use of *n*-$BuNH_2$ and pyrrolidine usually benefits SHC coupling,[11] *n*-$BuNH_2$ and pyrrolidine are apparently not suitable solvents for the present reaction, leading to a very complicated, unidentified product mixture. On the contrary, the use of dialkylamines such as $Et_2NH$, $Bu_2NH$, or piperidine leads to clean hydrodeiodo SHC reactions in high yields. However, the use of sterically hindered amine solvents such as $Et_3N$, *i*-$Pr_2NH$,[12] or *t*-$BuNH_2$ promotes fluorenyl derivative formation. For unknown reasons, the use of $(Me_3Si)_2NH$ completely retards the reaction, leaving the starting compound **3** untouched.

Significant ligand effects were also observed (Table 5) in this reaction. Similar to the normal SHC coupling reaction, this reaction is inhibited either by bidentate phosphine ligands or by excess phosphine ligands, implying the presence of a ligand-dissociation mechanism in the rate-determining step.[13,14] Complementary results were also observed when sterically hindered P(*o*-tolyl)$_3$

(7) Aromatic solvents are also commonly used in Sonogashira reactions. For examples, see: (a) Kajanus, J.; van Berlekom, S. B.; Albinsson, B.; Mårtensson, J. *Synthesis* **1999**, 1155. (b) Mongin, O.; Papamicaël, C.; Hoyler, N.; Gossauer, A. *J. Org. Chem.* **1998**, *63*, 5568. (c) Grosshenny, V.; Romero, F. M.; Ziessel, R. *J. Org. Chem.* **1997**, *62*, 1491.

(8) Luh, T.-Y.; Leung, M.-k.; Wong. K. T. *Chem. Rev.* **2000**, *100*, 3187.

(9) For examples, see: (a) Thorand, S.; Krause, N. *J. Org. Chem.* **1998**, *63*, 8551. (b) Miller, M. W.; Johnson, C. R. *J. Org. Chem.* **1997**, *62*, 1582. (c) Buszek, K. R.; Jeong, Y. *Synth. Commun.* **1994**, *24*, 2461.

(10) For examples, see: (a) Marshall, J. A.; DuBay, W. J. *J. Org. Chem* **1993**, *58*, 3602. (b) Hiyama, T.; Wakasa, N.; Ueda, T.; Kusumoto, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 640.

(11) The reactivity order of amines in Sonogashira coupling: *n*-$BuNH_2$ > $Et_3N$ > *i*-$Pr_2NH$ > $Et_2NH$ > $K_2CO_3$ and piperidine > pyrrolidine > *i*-$Pr_2NH$. For references, see: (a) Alami, M.; Ferri, F.; Iinstrumelle, G. *Tetrahedron Lett.* **1993**, *34*, 6403. (b) Beller, M.; Bolm, C. *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*; Wiley-VCH: Weinheim, 1998; Vol. 1, p 170.

(12) (a) McGaffin, G.; de Meijere, A. *Synthesis* **1994**, 583. (b) Scheuplien, S. W.; Harms, K.; Brückner, R.; Suffert, J. *Chem. Ber.* **1992**, *125*, 271.

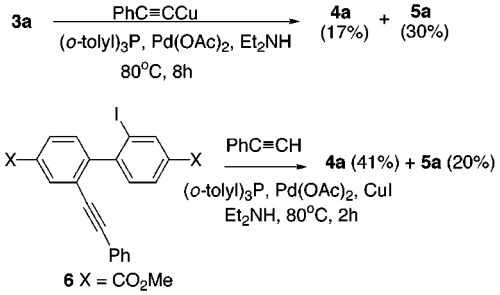
**Table 6. Effects of CuI on the Hydrodeiodo Phenylethynylation of 3[a]**

| ligand | CuI (%) | time (h) | **5a** (%) |
|---|---|---|---|
| $PPh_3$ | 0 | 4 | 37[b] |
| $PPh_3$ | 0.05 | 2 | 73 |
| $PPh_3$ | 0.19 | 20 | 15 |
| $PPh_3$ | 0.23 | 3.5 | 13 |
| P(*o*-tolyl)$_3$ | 0 | 2 | 29[c] |
| P(*o*-tolyl)$_3$ | 0.05 | 2 | 80 |

[a] Reagents used in these reactions: $Pd(OAc)_2$, $P(Ar)_3$, $Et_2NH$, CuI, at 80 °C. [b] **6**/SM = 37:63. [c] **6**/SM = 29:71.

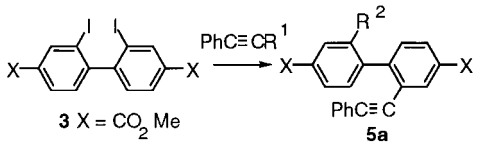
was used. Perhaps sterically hindered P(*o*-tolyl)$_3$ favors dissociation from a complex intermediate, giving rise to a coordinated, unsaturated Pd species for the catalytic reaction to proceed,[15] P(*o*-tolyl)$_3$ was found to be an extremely effective ligand in providing the hydrodeiodo SHC product.

Our results show that CuI is also an important catalyst for the reaction (Table 6). The best amounts of CuI/$Pd(OAc)_2$ were found empirically to be 5/10mol%. Although one might suspect that cuprous phenylacetylide was a possible key intermediate in the reaction,[16] this possibility was eliminated because the direct reaction of PhC≡CCu with **3** under similar conditions was relatively ineffective, with significant amounts of fluorenyl derivative **4a** isolated from the reaction. More interestingly, when monophenylethynyl iodide **6** was used in the reaction, **4a** was isolated as the major product. The inconsistent product distribution of **4a**/**5a** in comparison with the results that we obtained above clearly eliminates the possibility of **6** as the key intermediate in the hydrodeiodoethynylation. Therefore, we tentatively proposed that the SHC coupling step occurs after the hydrodeiodination step.




To elucidate the source of the hydrogen in the hydrodeiodination step, a series of deuterium isotope-labeling experiments were carried out, and their results are summarized in Table 7. First, we subjected PhC≡CD and **3** to the reaction under normal conditions, using $Et_2NH$ as the solvent; the main product was nondeuterated **5a**. Because there was no deuterium incorporated into the product, one might suspect that the aromatic hydrogen originates from $Et_2NH$. However, the possibility of a relatively fast hydrogen−deuterium (H/D) preexchange between $Et_2NH$ and PhC≡CD prior to the hydrodeiodination of **3** could not be eliminated. To examine the possibility of the H/D exchange mechanism, we subjected

**Table 7. Deuterium-Labeling Experiments for the Hydrodeiodo Phenylethynylation of 3[a]**




| $R^1$ | deuterated $R_2NH$ | $R^2$ = D (%) |
|---|---|---|
| D | $Et_2NH$ | 0 |
| D | piperidine-$d_{11}$ | 67 |
| H | piperidine-*N*-$d_1$ | 0 |
| H | piperidine-$d_{11}$ | 21 |
| D | piperidine-*N*-$d_1$ | 32 |

[a] Reagents used in these experiments: $Pd(OAc)_2$, P(*o*-tolyl)$_3$, $R_2NH$, CuI at 80 °C. [b] PhC≡CD (90%); piperidine-$d_{11}$ (98%).

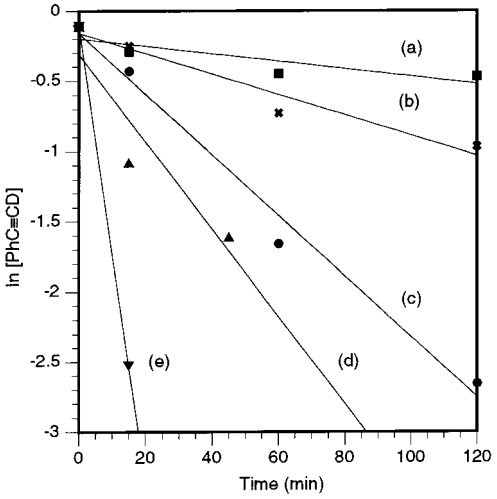



**Figure 1.** Chemical kinetics of H/D exchange between $Et_2NH$ and PhC≡CD in the presence of different catalysts at room temperature. (a) $Pd(OAc)_2$, (b) P(*o*-tolyl)$_3$, (c) $Pd(OAc)_2$/P(*o*-tolyl)$_3$, (d) CuI/P(*o*-tolyl)$_3$, (e) $Pd(OAc)_2$/P(*o*-tolyl)$_3$/CuI.

PhC≡CD to $Et_2NH$ in the presence of various combinations of $Pd(OAc)_2$, P(*o*-tolyl)$_3$, and CuI as the catalysts (Figure 1). The chemical kinetics of the H/D exchange at room temperature was followed by $^1H$ NMR spectroscopy. According to our results shown in Figure 1, the combination of CuI/P(*o*-tolyl)$_3$, $Pd(OAc)_2$/P(*o*-tolyl)$_3$, and $Pd(OAc)_2$/P(*o*-tolyl)$_3$/CuI is a good catalyst for the H/D exchange process. In particular, $Pd(OAc)_2$/P(*o*-tolyl)$_3$/CuI was found to be the most effective. Under these conditions, the H/D exchange is almost complete within a few minutes. These results explain why the nondeuterated product was isolated from this reaction. Because $Et_2NH$, the solvent, has a high concentration potential, the fast H/D exchange between the reagents may convert PhC≡CD to PhC≡CH before the hydrodeiodination proceeds. Fortunately, we discovered later that the H/D exchange between PhC≡CH(D) and piperidine-($d_0$, *N*-$d_1$, or $d_{11}$) is relatively slower than the H/D conversion; therefore, it is a reasonable solvent system for the isotope-labeling experiments.

Because piperidine-$d_{11}$ is commercially available, the first labeling study was carried out in piperidine-$d_{11}$ using PhC≡CD as the reagent (Table 7). In this case, up to 67% of deuterium incorporation in **5a** was observed. Incomplete deuterium incorporation could be partially explained by the relatively low purity of PhC≡CD (90%) and piperidine-$d_{11}$ (98%, Cambridge Isotopes Company). In addition, the discrepancy arising from deuterium

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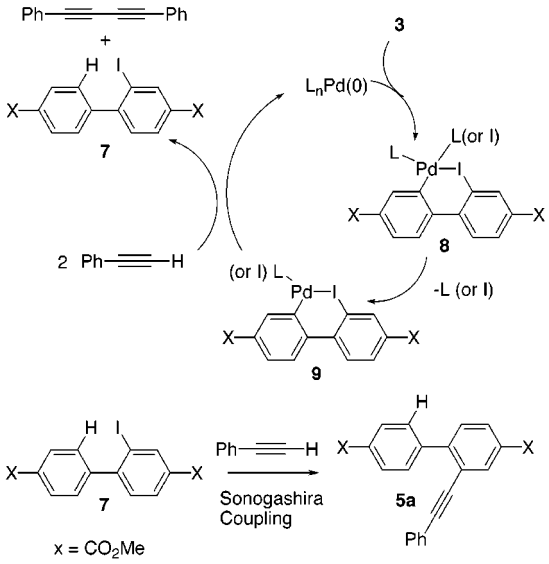
(15) (a) Louie, J.; Paul, F.; Hartwig, J. F. *Organometallics* **1996**, *15*, 2794. (b) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031.
(16) (a) Villemin, D.; Schigeko, E. *J. Organomet. Chem.* **1998**, *346*, C24. (b) Castro, C. E.; Stephens, R. D. *J. Org. Chem.* **1963**, *28*, 2163.

**Scheme 1**




kinetic isotope effects could not be ignored. Nevertheless, this result indicated that the hydrogen transferred to the aromatic ring in the hydrodeiodination mainly originates from either PhC≡CH or piperidine. On the other hand, when we employed PhC≡CH using piperidine-$N$-$d_1$ as the solvent (entry 3), only nondeuterated **5a** was obtained, according to the $^1$H NMR analysis. This observation implies that the aromatic hydrogen does not originate from the relatively acidic −NH− group. When the reaction proceeded in piperidine-$d_{11}$, only 21% deuterium incorporation was observed. Because the piperidine-$d_{11}$ solvent is the main component of the solution, its deuterium content should not be significantly altered by the H/D exchange process. Hence, if the hydrogen was transferred from piperidine to the aromatic ring, we would expect to obtain **5a** with a high deuterium content. However, the low extent of deuterium incorporation into the product indicates that the aromatic hydrogen may originate from phenylacetylene instead of from piperidine; H/D preexchange between piperidine-$d_{11}$ and phenylacetylene leads to about 21% of the deuterated product.

On the other hand, when PhC≡CD was reacted in piperidine-$N$-$d_1$, 32% deuterium incorporation was identified. As mentioned above, only 67% of deuterium incorporation in the final product was observed, even in the PhC≡CD/piperidine-$d_{11}$ system. Because H/D preexchange between PhC≡CD piperidine-$N$-$d_1$ may lead to PhC≡CH, we estimated that the H/D preexchange contributed about 35% of the nondeuterated product in this case.

To explain all of the observations about this unusual hydrodeiodo SHC coupling, a schematic diagram for the proposed mechanism was tentatively outlined in Scheme 1. However, the possibility of a mechanism involving a palladacycle intermediate could not be eliminated.[14] In our previous discussion, we proposed that the reduction of the first iodide on 2,2′-diiodobiphenyls would take place before the normal SHC coupling occurs. The hydrodeiodination product **7** in the first step would further react and lead to monophenylethynyl product **5a**. In our proposed mechanism, a Pd(0) complex may first oxidatively insert into one of the C−I bonds of **3** to give intermediate **8**.[4] Perhaps because of the ligation of the Pd(II) center with the adjacent iodine atom[17] the palladium intermediate behaves differently than normal SHC intermediates do, preferentially leading to **7**. In the meantime, 2 equiv of PhC≡CH were coupled to give PhC≡C−C≡CPh, releasing Pd(0) back into the catalytic cycle. Finally, the SHC coupling of **7** with PhC≡CH leads to the product **5a**. This proposed mechanism is also consistent with the observed ligand effects. Bidentate phosphine ligands occupy the coordination sites of the intermediate complex **8**, preventing the Pd species from further reaction. On the other hand, bulky ligands such as P(*o*-tolyl)$_3$ favor dissociation to **9**, creating an empty site for further coordination and reaction.

## Experimental Section

**General Methods and Materials.** Pd(OAc)$_2$, phosphine ligands, phenylacetylene, CuI, HNEt$_2$, NEt$_3$, and piperidine-$d_{11}$ were obtained commercially (Aldrich, Acros, Tokyo Kasei, CIL). Pd(OAc)$_2$, phosphine ligands, CuI, and piperidine-$d_{11}$ were used as received. Amines were dried over CaH and distilled before use. Dimethyl 2,2′-diiodobiphenyl-4,4′-dicarboxylate,[3a] 1-ethynyl-4-octyloxybenzene,[18] 1-ethynyl-4-methoxybenzene,[19] 1-ethynyl-4-nitrobenzene,[20] piperidine-$N$-$d_1$,[21] and PhC≡CD[21] were prepared according to literature procedures.

**Typical Procedure for the Preparation of 5.** To a solution of dimethyl 2,2′-diiodobiphenyl-4,4′-dicarboxylate (**3**) (200 mg, 0.38 mmol), Pd(OAc)$_2$ (8.9 mg, 10 mol %), P(*o*-tolyl)$_3$ (23 mg, 20 mol %), and CuI (3.6 mg, 5 mol %) in dry HNEt$_2$ (3 mL) was added PhC≡CH (0.1 mL, 1 mmol) under Ar, and the mixture was reacted at 80 °C for 2 h. Water was added to quench the reaction, and the mixture was extracted with $CHCl_3$ several times. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was further purified by column chromatography on silica gel using hexanes/EtOAc (8:1) as the eluent to obtain **5a**.

**Dimethyl 2-phenylethynylbiphenyl-4,4′-dicarboxylate (5a):** colorless solid (83%), mp: 170−171 °C; $^1$H NMR ($CDCl_3$) $\delta$ 8.32 (d, $J$ = 1.6 Hz, 1H), 8.13 (d, $J$ = 8.3 Hz, 2H), 8.02 (dd, $J$ = 8.1, 1.6 Hz, 1H), 7.75 (d, $J$ = 8.3 Hz, 2H), 7.49 (d, $J$ = 8.1 Hz, 1H), 7.28−7.32 (m, 5H), 3.95 (s, 3H), 3.94 (s, 3H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 165.90, 165.19, 145.81, 143.21, 133.36, 131.15, 130.21, 129.50, 129.45, 129.41, 129.38, 129.13, 129.00, 128.75, 121.71, 121.04, 93.11, 87.50, 52.44, 52.24; IR 1728 cm$^{-1}$; HRMS (EI) $m/z$ 370.1196, calcd for $C_{24}H_{18}O_4$ 370.1205. Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.61; H, 4.94.

**Dimethyl 2-(4-octyloxy)phenylethynylbiphenyl-4,4′-dicarboxylate (5b).** Treatment of **3** (3.0 g) with 1-ethynyl-4-octyloxybenzene (2.9 g) gave a crude solid. Purification by liquid chromatography on silica gel (eluent: hexanes/EtOAc 6:1) afforded essentially pure **5b** as a colorless solid (1.9 g, 66%), mp: 88−89 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 8.16 (d, $J$ = 1.6 Hz, 1H), 8.10 (d, $J$ = 8.3 Hz, 2H), 8.01 (dd, $J$ = 8.1, 1.6 Hz, 1H), 7.85 (d, $J$ = 8.3 Hz, 2H), 7.67 (d, $J$ = 8.1 Hz, 1H), 7.31 (d, $J$ = 8.7 Hz, 2H), 6.93 (d, $J$ = 8.7 Hz, 2H), 3.96 (t, $J$ = 6.4 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 1.65−1.72 (m, 2H), 1.15−1.45 (m, 9H), 0.84 (t, $J$ = 6.6 Hz, 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.91, 166.23, 159.49, 146.18, 144.25, 134.04, 132.88, 129.60, 129.56, 129.50, 129.31, 129.25, 128.92, 122.45, 114.58, 114.52, 93.77, 86.56, 68.08, 52.31, 52.17, 31.77, 29.30, 29.19, 29.12, 25.97,

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22.62, 14.06.; IR 2207, 1722 $cm^{-1}$; HRFAB *m/z* 498.2421, calcd for $C_{32}H_{34}O_5$ 498.2406. Anal. Calcd for $C_{32}H_{34}O_5$: C, 77.08; H, 6.87. Found: C, 76.82; H. 6.87.

**9-[Bis(4-octyloxyphenyl)prop-2-ynylidene]-9H-fluorene-2,7-dicarboxylic acid dimethyl ester (4b):** light yellow solid (0.58 g, 14%), mp: 115−116 °C; $^1$H NMR ($CDCl_3$) $\delta$ 9.68 (s, 1H), 8.11 (d, $J$ = 7.9 Hz, 1H), 7.91 (d, $J$ = 7.9 Hz, 1H), 7.79 (d, $J$ = 8.0 Hz, 1H), 7.72 (d, $J$ = 8.0 Hz, 1H), 7.66 (d, $J$ = 8.9 Hz, 2H), 7.46 (d, $J$ = 8.7 Hz, 2H), 7.34 (s, 1H), 7.03 (d, $J$ = 8.7 Hz, 2H), 6.90 (d, $J$ = 8.9 Hz, 2H), 4.05 (t, $J$ = 6.6 Hz, 2H), 3.98 (t, $J$ = 6.6 Hz, 2H), 3.94 (s, 3H), 3.75 (s, 3H), 1.85−1.76 (m, 4H), 1.37−1.28 (m, 24H), 0.91−0.86 (m, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 167.19, 166.84, 160.17, 159.86, 142.56, 142.43, 139.07, 138.58, 136.76, 133.68, 131.34, 130.33, 129.95, 129.56, 129.27, 128.95, 126.76, 126.47, 126.01, 119.89, 119.87, 114.97, 114.76, 114.68, 105.03, 91.18, 68.24, 68.17, 52.05, 51.85, 31.84, 31.79, 29.40, 29.34, 29.31, 29.27, 29.22, 29.17, 26.13, 26.00, 22.67, 22.64, 14.10, 14.08; IR 2170, 1727, 1717 $cm^{-1}$; HRFAB *m/z* 726.3892, calcd for $C_{48}H_{54}O_6$ 726.3920.

**Dimethyl 2-(4-methoxy)phenylethynylbiphenyl-4,4′-dicarboxylate (5c).** Treatment of **3** (1.0 g) with 1-ethynyl-4-methoxybenzene (0.61 g) gave a crude solid. Purification by chromatography on silica gel (eluent: hexanes/EtOAc 6:1) afforded essentially pure **5c** as a colorless solid (0.45 g, 60%), mp: 141−142 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 8.17 (d, $J$ = 1.8 Hz, 1H), 8.11 (d, $J$ = 8.5 Hz, 2H), 8.02 (dd, $J$ = 7.9, 1.8 Hz, 1H), 7.85 (d, $J$ = 8.5 Hz, 2H), 7.68 (d, $J$ = 7.9 Hz, 1H), 7.34 (d, $J$ = 8.9 Hz, 2H), 6.96 (d, $J$ = 8.9 Hz, 2H), 3.91 (s, 3H), 3.90 (s, 3H), 3.77 (s, 3H); $^{13}$C NMR ($CDCl_3$): $\delta$ 166.93, 166.25, 159.91, 164.25, 144.27, 134.07, 132.93, 129.64, 129.59, 129.54, 129.34, 129.28, 128.99, 122.42, 114.85, 114.09, 93.65, 86.68, 55.31, 52.35, 52.21; IR 2209, 1730 $cm^{-1}$; HRFAB *m/z* 400.1301, calcd for $C_{25}H_{20}O_5$ 400.1310.

**Dimethyl 2-(4-Nitro)phenylethynylbiphenyl-4,4′-dicarboxylate (5d).** Treatment of **3** (1.0 g) with 1-ethynyl-4-nitrobenzene (0.68 g) gave a crude solid. Purification by liquid chromatography on silica gel (eluent: hexanes/EtOAc 6:1) afforded essentially pure **5d** as a colorless solid (0.16 g, 20%), mp: 230−231 °C; $^1$H NMR ($CDCl_3$) $\delta$ 8.34 (d, $J$ = 1.3 Hz, 1H), 8.08−8.18 (m, 5H), 7.71 (d, $J$ = 8.4 Hz, 2H), 7.52 (d, $J$ = 7.8 Hz, 1H), 7.43 (d, $J$ = 8.9 Hz, 2H), 3.96 (s, 3H), 3.95(s, 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.74, 165.92, 147.17, 147.12, 143.76, 134.58, 132.10, 130.36, 130.04, 129.84, 129.77, 129.55, 129.41, 129.27, 123.68, 120.94, 92.95, 91.25, 52.48, 52.31; IR 1719 $cm^{-1}$; HRFAB *m/z* 415.1038, calcd for $C_{24}H_{17}O_6N$ 415.1055.

**Preparation of 9-Diphenylprop-2-ynylidene-9H-fluorene-2,7-dicarboxylic acid dimethyl ester (4a).** To a solution of dimethyl 2,2′-diiodobiphenyl-4,4′-dicarboxylate (**3**) (200 mg, 3.8 mmol), $Pd(OAc)_2$ (8.9 mg, 10 mol %), $Ph_3P$ (20.1 mg, 20 mol %), and CuI (3.6 mg, 5 mol %) in dry $NEt_3$ (3 mL) was added phenylacetylene (10 mmol) under Ar, and the mixture was stirred at 80 °C for 2 h. Water was added to quench the reaction, and the mixture was extracted with $CHCl_3$. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was further purified by column chromatography on silica gel, using hexane/AcOEt (8:1) as the eluent, to afford **4a** as a slightly yellow solid (81%), mp: 229−230 °C; $^1$H NMR ($CDCl_3$) $\delta$ 9.65 (s, 1H), 8.11 (d, $J$ = 6.8 Hz, 1H), 7.88 (d, $J$ = 6.8 Hz, 1H), 7.67−7.76 (m, 4H), 7.54 (s, 5H), 7.39 (t, $J$ = 2.2 Hz, 3H), 7.13 (s, 1H), 3.91 (s, 3H), 3.74 (s, 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 167.00, 166.66, 142.79, 142.72, 139.09, 138.78, 138.27, 138.16, 132.00, 130.42, 129.71, 129.64, 129.27, 129.17, 129.04, 128.85, 128.72, 128.44, 126.98, 126.12, 125.69, 122.81, 119.92, 104.45, 91.41, 52.02, 51.89; IR 2183, 1720, 1710 $cm^{-1}$; HRFAB *m/z* 470.1530, calcd for $C_{32}H_{22}O_4$ 470.1518.

**2-Iodo-2′-phenylethynylbiphenyl-4,4′-dicarboxylic acid dimethyl ester (7).** To a solution of dimethyl 2,2′-diiodobiphenyl-4,4′-dicarboxylate (1.99 g, 3.8 mmol) and cuprous phenylacetylide (0.62 g, 3.8 mmol) in dry pyridine (25 mL) under Ar, and the mixture was stirred at 110 °C for 20 h. Water was added, and the mixture was extracted with $CH_2Cl_2$. The combined organic layer was dried over anhydrous $MgSO_4$ and evaporated. The crude product was further purified by column chromatography on silica gel using hexane/AcOEt (10:1) as the eluent to give a colorless solid (14%), mp: 114−115 °C. $^1$H NMR ($CD_3COCD_3$) $\delta$ 8.60 (d, $J$ = 1.6 Hz, 1H), 8.23 (d, $J$ = 1.8 Hz, 1H), 8.14 (dd, $J$ = 8.0, 1.6 Hz, 1H), 8.11 (dd, $J$ = 8.0, 1.8 Hz, 1H), 7.55 (d, $J$ = 8.0 Hz, 1H), 7.48 (d, $J$ = 8.0 Hz, 1H), 7.30−7.33 (m, 3H), 7.20−7.22 (m, 2H), 3.96 (s, 3H), 3.93 (s, 3H); $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 166.26, 165.55, 150.69, 150.35, 140.52, 133.39, 132.25, 132.11, 131.41, 131.10, 130.66, 129.93, 129.76, 129.72, 129.40, 123.84, 123.32, 98.81, 94.78, 87.68, 52.78, 52.72; HRFAB *m/z* ($M^+$) 496.0182, ($M^+ + 1$) 497.0268; calcd for $C_{24}H_{17}O_4I$ 496.0172, calcd for $C_{24}H_{18}O_4I$ 497.0250.

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**Supporting Information Available:** ORTEP of **4a**, $^1$H and $^{13}$C NMR spectra of **4a**, **4b**, **5a**−**5d**, and **7**, and $^1$H, $^{13}$C, NOESY, $^1$H−$^1$H COSY, HMBC, and HMQC NMR spectra of **5a**-$d_1$. This material is available free of charge via the Internet at http://pubs.acs.org.

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