Palladium-Catalyzed Coupling Reactions of Biphenylene with Olefins, Arylboronic Acids, and Ketones Involving C−C Bond Cleavage

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The reaction of biphenylene with olefins in the presence of $Pd(PPh_3)_4$ leads to the catalytic formation of products arising from addition of the vinylic C−H bond across the carbon−carbon bond of biphenylene. Weak acids are found to promote the reaction. Under similar conditions, arylboronic acids lead to products in which an aryl group adds across the C−C bond. Ketones and nitriles possessing α-hydrogens are found to also add across the C−C bond of biphenylene, resulting in the formation of new biaryl derivatives.

Introduction

The activation and functionalization of C−C bonds by soluble transition metal complexes has been of current interest in organometallic chemistry. Although various stoichiometric reactions involving C−C bond cleavage with transition metal complexes have been developed,[1] the catalytic versions have been less explored.[2] Our group has recently reported the catalytic C−C bond activation and functionalization of biphenylene under nickel, palladium, or platinum catalysis.[2o,r,u,v] In the reaction, oxidative addition of biphenylene toward the zerovalent metal species gives a key metalacyclic intermediate, $L_nM(2,2'\text{-biphenyl})$ (M = Ni, Pd, or Pt). Then, insertion of small molecules such as alkynes, carbon monoxide, and isocyanides into one of the aryl−metal bonds followed by reductive elimination produces the corresponding coupling products.[2u,v] Meanwhile, the ring opening of metalacyclic compounds by acidic reagents has been of interest as the reverse of the cyclometalation reaction, and many recent studies have been devoted to the development of new systems and the investigation of their mechanisms.[3,4] Interestingly, it has been found that the addition of acidic reagents such as *p*-cresol and acetic acid enables biphenylene to undergo new coupling reactions; in the presence of the acids, palladium-catalyzed cross-coupling of biphenylene with olefins, arylboronic acids, and ketones occurred efficiently. The findings are reported herein.

Results and Discussion

When a mixture of biphenylene (**1**) (0.1 mmol) and butyl acrylate (**2**, R = CO_2Bu^n)(0.13 mmol) was heated in the presence of $Pd(PPh_3)_4$ (0.005 mmol) and *p*-cresol (0.1 mmol) in C_6D_6 (0.7 cm^3) under N_2 at 120 °C for 6 days, butyl 3-(1,1′-biphenyl-2-yl)-2-propenoate (**3**) was produced in a yield of 93% (GC yield, 71% isolated yield, *E*:*Z* = 87:13). A minor amount of **1** (2%) was transformed into the homocoupling product, tetraphenylene.[2o] The addition of *p*-cresol was found to be essential for the high-yield cross-coupling; in its absence, **1** was predominantly converted to tetraphenylene (55%) and the yield of **3** was low (13%). A relatively stronger acid, acetic acid, completely suppressed the homocoupling, although the yield of **3** somewhat decreased to 78%. Under the conditions employing *p*-cresol, other olefins

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(3) Two reviews have been published: (a) Canty, A.; van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406. (b) Cámpora, J.; Palma, P.; Carmona, E. *Coord. Chem. Rev.* **1999**, *193*−*195*, 207.

(4) (a) Bocelli, B.; Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1984**, *279*, 225. (b) Larock, R. C.; Johnson, P. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1368. (c) Markies, B. A.; Wijkens, P.; Kooijman, H.; Spek, A. L.; Boersma, J.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1420. (d) Catellani, M.; Ferioli, L. *Synthesis* **1996**, 769. (e) Catellani, M.; Marmiroli, B.; Fagnola, M. C.; Acquotti, D. *J. Organomet. Chem.* **1996**, *507*, 157. (f) Catellani, M.; Cugini, F.; Bocelli, G. *J. Organomet. Chem.* **1999**, *584*, 63. (g) Cámpora, J.; López, J. A.; Palma, P.; Valerga, P.; Spillner, E.; Carmona, E. *Angew. Chem., Int. Ed.* **1999**, *38*, 147. (h) Oguma, K.; Miura, M.; Satoh, T.; Nomura, M. *J. Am. Chem. Soc.* **2000**, *122*, 10464.

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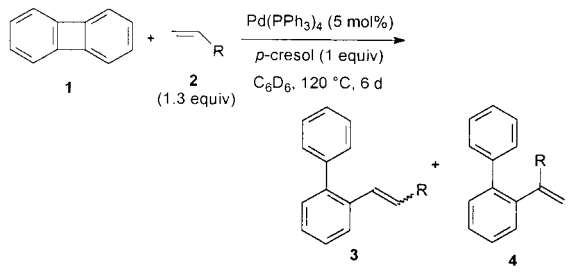
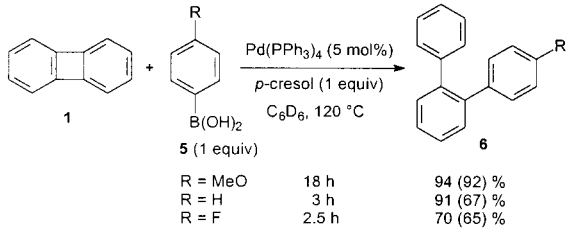
such as 4-methylstyrene and styrene, also underwent cross-coupling with **1** to produce **3**, 2-[2-(4-methylphenyl)ethenyl]-1,1′-biphenyl, and 2-(2-phenylethenyl)-1,1′-biphenyl, respectively, as *E*/*Z* mixtures. In these cases, minor amounts of 1,1-diaryl ethene isomers **4** were also formed.



(1)

Under similar conditions, biphenylene was found to be coupled with arylboronic acids. As shown in eq 2, treatment of **1** (0.1 mmol) with 4-methoxyphenylboronic acid (**5**, R = OMe) (0.1 mmol) in the presence of $Pd(PPh_3)_4$ (0.005 mmol) and *p*-cresol (0.1 mmol) in C_6D_6 under N_2 at 120 °C for 18 h gave 4-methoxy-1,1′:2′,1″-terphenyl (**6**) in a yield of 94%. Without the addition of

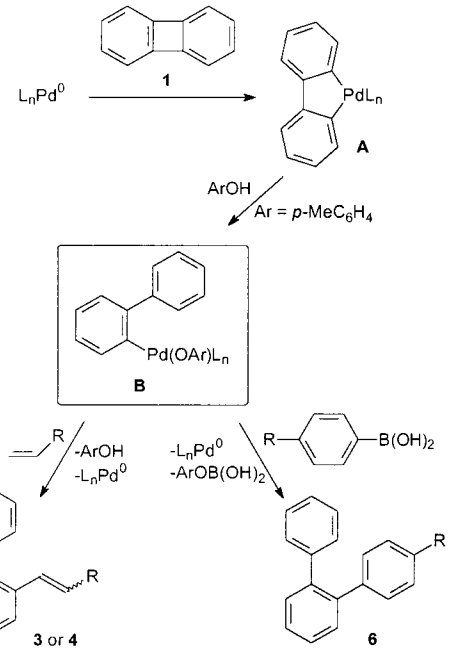


(2)

p-cresol, the product yield was reduced to 66%, and again 10% of **1** was converted to tetraphenylene. Two other boronic acids, phenylboronic acid and 4-fluorophenylboronic acid, can also be used in the reaction to afford the corresponding terphenyls **6** in 91 and 70% yields, respectively.

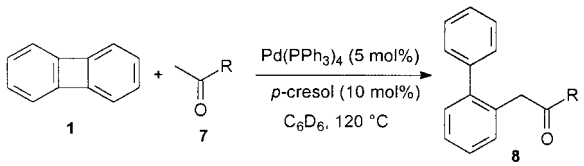
The palladium-catalyzed cross-coupling reactions of aryl halides with olefins and arylboronic acids are well known as Heck and Suzuki reactions, respectively, and have been widely used for organic synthesis.[5] In these reactions, arylpalladium species, which can be formed by oxidative addition of aryl halides toward Pd^0 species, have been considered as a common intermediate. It is also possible that a similar arylpalladium intermediate is involved in the present reactions (Scheme 1). As in the homocoupling or hydrogenolysis of biphenylene under palladium catalysis,[2o,r] oxidative addition of biphenylene toward Pd^0 species gives a (2,2′-biphenyl)-palladium species **A**. In the presence of *p*-cresol, **A** may undergo protonolysis by the acid to form a key intermediate, aryl(aryloxy)palladium species **B**, which reacts with olefins **2** and arylboronic acids **5** in a manner similar to that in the reactions of aryl halides. A similar

Scheme 1



protonolysis of a palladacycle by a phenolic compound has been observed.[4f] However, another pathway via a hydridopalladium species formed from a Pd(0) complex and acid, prior to the C−C bond activation of **1**, cannot be excluded at the present stage.[6] In the absence of any acidic species, **A** may predominantly react with another molecule of **1** to form the homocoupling product, tetraphenylene.[2o] The fact that the cross-coupling of **1** with 4-methoxyphenylboronic acid **5** proceeded moderately even without additional acids may indicate that, in this case, the boronic acid itself or water formed in its dehydration can act as the acid.[4h]

Recently, it has been reported that ketones such as acetophenone can react with aryl halides under the mild conditions similar to those for the Heck reaction to form the corresponding α-arylated ketones.[7] Therefore, we next investigated the reaction of biphenylene with ketones (eq 3). When biphenylene (**1**) (0.1 mmol) was



(3)

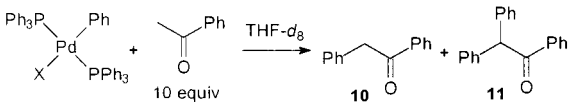
treated with acetophenone (**7**, R = Ph) (0.1 mmol) in the presence of $Pd(PPh_3)_4$ (0.005 mmol) and *p*-cresol (0.1

(5) (a) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985. (b) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons Ltd.: Chichester, 1995. (c) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (d) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1997.

(6) A large number of hydridopalladium species have been reported in the literature, for example: (a) Shunn, R. A. *Inorg. Chem.* **1976**, *15*, 208. (b) Zudin, V. N.; Chinakov, V. D.; Nekipelov, V. M.; Likholobov, V. A.; Yermakov, Y. I. *J. Organomet. Chem.* **1985**, *289*, 425. (c) Di Bugno, C.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390. (d) Seligson, A. L.; Cowan, R. L.; Trogler, W. C. *Inorg. Chem.* **1991**, *30*, 3371. (e) Kushino, Y.; Itoh, K.; Miura, M.; Nomura, M. *J. Mol. Catal.* **1994**, *89*, 151. (f) Yamamoto, Y.; Radhakrishnan, U. *Chem. Soc. Rev.* **1999**, *28*, 199. (g) Eastham, G. R.; Heaton, B. T.; Iggo, J. A.; Tooze, R. P.; Whyman, R.; Zacchini, S. *Chem. Commun.* **2000**, 609. (h) Perez, P. J.; Calabrese, J. C.; Bunel, E. E. *Organometallics* **2001**, *20*, 337, and references therein.

mmol) in C_6D_6 under N_2 at 120 °C for 1 day, 2-(1,1′-biphenyl-2-yl)-1-phenylethanone (**8**) was produced in a yield of 33%, and 62% of **1** was recovered. The use of acetic acid in place of *p*-cresol completely inhibited the reaction, and **1** was recovered quantitatively. Interestingly, when the amount of *p*-cresol was reduced to 0.01 mmol, the yield of **8** was significantly improved up to 76%. The use of 2 equiv of acetophenone (0.2 mmol) brought a higher reaction rate and a further increase of the product yield (84% after 7 h). Without the addition of the acids, **1** was converted to a mixture of **8** (24%) and tetraphenylene (39%). Other methyl ketones, 2-acetylthiophene and pinacolone, also reacted with **1** under similar conditions using the reduced amount of *p*-cresol to produce the corresponding substituted biphenyls in good yields.

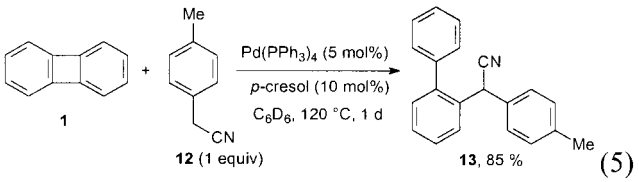
In the reaction of **1** with methyl ketones **7** in the presence of *p*-cresol, the intermediate **B** in Scheme 1 may also be involved as in the reactions using olefins and arylboronic acids. In this case the aryloxy ligand seems to act as base to remove an α-proton of the ketones.[8] When acetic acid is used, an aryl(acetate)-palladium species should be formed in place of **B**. Taking into account the result that the coupling was not initiated by this acid, it is possible that the acetate ligand may not be a strong enough base to eliminate the proton. The difference in reactivity between these species was also confirmed by stoichiometric reactions of the corresponding phenylpalladium complexes (eq 4). Thus, *trans*-Ph(AcO)Pd(PPh_3)$_2$ (**9a**) and *trans*-Ph(*p*-



(4)

MeC_6H_4O)Pd(PPh_3)$_2$ (**9b**) were heated with an excess amount (10 equiv) of acetophenone in THF-d_8 under N_2. At 50 °C, while **9a** showed no changes in its NMR signals, **9b** gave 1,2-diphenylethanone (**10**) in 51% yield, along with a small amount of diphenylated product **11** (7%) after 18 days. Even when heated at 80 °C, most of **9a** was recovered: only 6% of **10** was detected after 21 days.

The use of 1 equiv of *p*-cresol, an excess amount toward the palladium complex, reduced the yield of **8**, while it efficiently promoted the reactions with olefins and arylboronic acids. The reason for the former result is not clear at the present stage. It is possible that other molecules of *p*-cresol may interact with the intermediate **B** to retard the following substitution of the α-proton of **7**.[6c,d,8,9] Meanwhile, the treatment of 1,2-diphenylethanone with **1** in the presence or absence of *p*-cresol did not generate any cross-coupling products, although the benzyl ketone was a good substrate for the coupling with aryl halides.[7a,e] Under the present nearly neutral conditions, in contrast to the basic conditions generally used for the reaction with aryl halides, the acidity of starting molecules appears to be an important factor affecting the reaction efficiency. The presence of an acidic ketone (pK_a = 17.6 in DMSO at 25 °C)[10] might inhibit the coupling reaction in a manner[9d,f] similar to excess *p*-cresol (pK_a value of phenol is around 18).[10] It is found that even the reaction of **1** with acetophenone is completely inhibited by the addition of 1 equiv of 1,2-diphenylethanone. On the other hand, phenylacetonitriles are known to possess lower acidity (pK_a = 22),[10] which is rather comparable to that of acetophenone (pK_a = 24.7).[10] Indeed, 4-methylphenylacetonitrile (**12**) reacted with **1** smoothly under the same conditions as those for the reaction of acetophenone to give the cross-coupling product **13** in 85% yield (eq 5). The thermo-



(5)

dynamics of equilibration of various metal−X species on Pt and Ru have been extensively studied and provide evidence for the facile equilibration of these species.[11]

Experimental Section

All manipulations were performed under N_2 atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation glovebox. All NMR spectra were recorded at 400 MHz in $CDCl_3$ as solvent, unless otherwise noted. All ^{1}H and ^{13}C chemical shifts are reported in ppm (δ) relative to TMS and referenced using chemical shifts of residual solvent resonances (^{1}H THF-d_8 δ 1.73, $CDCl_3$ δ 7.24; ^{13}C $CDCl_3$ δ 77.0). ^{31}P NMR spectra were referenced to external 30% H_3PO_4 (δ 0.0). MS data were obtained by EI. GLC analysis was carried out with a CBP-1 capillary column (i.d. 0.25 mm × 15 m). Pd(PPh_3)$_4$,[5a] *trans*-Ph(I)Pd(PPh_3)$_2$,[12] and biphenylene (**1**)[13] were prepared by the methods reported previously. Other starting materials were

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(8) It has been reported that an aryloxygold(III) species can abstract a proton from methyl cyanoacetate, malononitrile, and phenyl acetylene: Sone, T.; Iwata, M.; Kasuga, N.; Komiya, S. *Chem. Lett.* **1991**, 1949.

(9) A reported property of late transition metal alkoxides is their ability to associate with alcohols and so form adducts through O−H···O hydrogen bonding. The association is known to be strong when the R group of an alcohol, ROH, is an electron-withdrawing unit: (a) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563. (b) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096. (c) Osakada, K.; Ohshiro, K.; Yamamoto, A. *Organometallics* **1991**, *10*, 404. (d) Osakada, K.; Kim, Y.-J.; Tanaka, M.; Ishiguro, S.; Yamamoto, A. *Inorg. Chem.* **1991**, *30*, 197. (e) Simpson, R. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 781. (f) Kapteijn, G. M.; Dervisi, A.; Grove, D. M.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 10939. (g) Kapteijn, G. M.; Spee, M. P. R.; Grove, D. M.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 1405. (h) Kim, Y.-J.; Lee, J.-Y.; Osakada, K. *J. Organomet. Chem.* **1998**, *558*, 41.

(10) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(11) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444. Bryndza, H. E.; Domaille, P. J.; Tam, W.; Fong, L. K.; Paciello, R. A.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 1441.

(12) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.

(13) Yates, P. *Organic Synthesis*; Wiley: New York, 1968; Vol. 48, p 12.

commercially available. Solvents were purified by standard methods before use.

Catalytic Cross-Coupling of Biphenylene (1) with Olefins 2. A mixture of **1** (15 mg, 0.1 mmol), **2** (0.13 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), *p*-cresol (11 mg, 0.1 mmol), and C_6D_6 (0.7 cm^3) was placed in a resealable NMR tube. An N_2 atmosphere was charged, and the mixture was heated at 120 °C for 6 days. After cooling, the products were isolated by thin-layer chromatography on silica gel using hexanes−ethyl acetate as eluent.

Butyl 3-(1,1′-biphenyl-2-yl)-2-propenoate (*E*:*Z* = 87:13): ^{1}H NMR δ 7.71 (d, 1 H, J = 15.9 Hz, *E*), 7.68−7.70 (m, 1 H), 7.34−7.44 (m, 6 H), 7.28−7.31 (m, 2 H), 6.83 (d, 1 H, J = 12.2 Hz, *Z*), 6.38 (d, 1 H, J = 15.9 Hz, *E*), 5.91 (d, 1 H, J = 12.2 Hz, *Z*), 4.13 (t, 2 H, J = 6.6 Hz, *E*), 4.07 (t, 2 H, J = 6.6 Hz, *Z*), 1.58−1.65 (m, 2 H, *E*), 1.49−1.54 (m, 2 H, *Z*), 1.31−1.41 (m, 2 H, *E*), 1.21−1.27 (m, 2 H, *Z*), 0.91 (t, 3 H, J = 7.4 Hz, *E*), 0.85 (t, 3 H, J = 7.4 Hz, *Z*); ^{13}C NMR δ 166.9, 143.6, 142.9, 139.9, 132.6, 130.5, 129.8 (overlapped), 128.2, 127.6, 127.5, 126.7, 119.1, 64.2, 30.7, 19.1, 13.7; MS m/z 280 (M^+). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.21; H, 7.35.

(*E*)-2-[2-(4-Methylphenyl)ethenyl]-1,1′-biphenyl:[14] ^{1}H NMR δ 7.75 (d, 1 H, J = 7.6 Hz), 7.32−7.44 (m, 8 H), 7.26 (d, 2 H, J = 8.1 Hz), 7.10 (d, 2 H, J = 8.1 Hz), 7.07 (d, 1 H, J = 16.2 Hz), 7.01 (d, 1 H, J = 16.2 Hz), 2.32 (s, 3 H); ^{13}C NMR δ 141.0, 140.9, 137.4, 135.6, 134.8, 130.3, 130.0, 129.4, 129.3, 128.1, 127.5, 127.3, 127.0, 126.8, 126.4, 125.7, 21.2; MS m/z 270 (M^+).

(*E*)-2-(2-Phenylethenyl)-1,1′-biphenyl:[14] ^{1}H NMR δ 7.76 (d, 1 H, J = 7.5 Hz), 7.33−7.45 (m, 10 H), 7.29 (t, 2 H, J = 7.2 Hz), 7.21 (t, 1 H, J = 7.2 Hz), 7.12 (d, 1 H, J = 16.3 Hz), 7.04 (d, 1 H, J = 16.3 Hz); ^{13}C NMR δ 141.1, 140.9, 137.6, 135.4, 130.3, 130.0, 129.4, 128.6, 128.1, 127.8, 127.6, 127.5, 127.5, 127.1, 126.5, 125.8; MS m/z 256 (M^+).

Catalytic Cross-Coupling of Biphenylene (1) with Arylboronic Acids 5. The procedures were essentially the same as those for the reaction with **2**, other than the reaction time (2.5−18 h).

4-Methoxy-1,1′:2′,1″-terphenyl:[15] ^{1}H NMR δ 7.37−7.42 (m, 4 H), 7.19−7.23 (m, 3 H), 7.14−7.17 (m, 2 H), 7.05 (d, 2 H, J = 8.7 Hz), 6.75 (d, 2 H, J = 8.7 Hz), 3.76 (s, 3 H); ^{13}C NMR δ 158.3, 141.7, 140.4, 140.1, 133.9, 130.9, 130.6, 130.5, 129.8, 127.9, 127.4, 127.1, 126.3, 113.3, 55.1; MS m/z 260 (M^+).

1,1′:2′,1″-Terphenyl:[15] ^{1}H NMR δ 7.39−7.44 (m, 4 H), 7.18−7.21 (m, 6 H), 7.12−7.14 (m, 4 H); ^{13}C NMR δ 141.5, 140.5, 130.6, 129.9, 127.8, 127.5, 126.4; MS m/z 230 (M^+).

4-Fluoro-1,1′:2′,1″-terphenyl:[15] ^{1}H NMR δ 7.39−7.41 (m, 4 H), 7.17−7.23 (m, 3 H), 7.05−7.12 (m, 4 H), 6.87−6.92 (m, 2 H); ^{13}C NMR δ 161.7 (d, J_{C-F} = 245.3 Hz), 141.3, 140.6, 139.5, 137.4, 131.3 (d, J_{C-F} = 7.8 Hz), 130.6, 130.5, 129.8, 127.9, 127.6, 127.5, 126.5, 114.8 (d, J_{C-F} = 21.2 Hz); MS m/z 248 (M^+).

Catalytic Cross-Coupling of Biphenylene (1) with Ketones 7 and Nitrile 12. A mixture of **1** (15 mg, 0.1 mmol), **7** or **12** (0.1−0.3 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), *p*-cresol (1 mg, 0.01 mmol), and C_6D_6 (0.7 cm^3) was placed in a resealable NMR tube. An N_2 atmosphere was charged, and the mixture was heated at 120 °C for 7 h to 3 days. After cooling, the products were isolated by thin-layer chromatography on silica gel using hexanes−ethyl acetate as eluent.

2-(1,1′-Biphenyl-2-yl)-1-phenylethanone: ^{1}H NMR δ 7.76−7.79 (m, 2 H), 7.47−7.52 (m, 1 H), 7.26−7.39 (m, 11 H), 4.24 (s, 2 H); ^{13}C NMR δ 198.3, 142.3, 141.3, 136.6, 133.0, 132.3, 130.6, 130.2, 129.1, 128.5, 128.3, 128.2, 127.6, 127.1, 127.0, 43.2; MS m/z 272 (M^+). Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.27; H, 5.88.

2-(1,1′-Biphenyl-2-yl)-1-(2-thienyl)ethanone: ^{1}H NMR δ 7.56 (dd, 1 H, J = 0.96, 4.9 Hz), 7.27−7.40 (m, 10 H), 7.00 (dd, 1 H, J = 4.0, 4.9 Hz), 4.17 (s, 2 H); ^{13}C NMR δ 190.9, 143.9, 142.3, 141.2, 133.7, 132.2, 132.0, 130.6, 130.1, 129.2, 128.2, 127.9, 127.6, 127.2, 127.1, 43.7; MS m/z 278 (M^+). Anal. Calcd for $C_{18}H_{14}OS$: C, 77.67; H, 5.07. Found: C, 77.62; H, 5.35.

1-(1,1′-Biphenyl-2-yl)-3,3-dimethylbutan-2-one:[16] ^{1}H NMR δ 7.24−7.37 (m, 5 H), 7.18−7.25 (m, 3 H), 7.14−7.16 (m, 1 H), 3.77 (s, 2 H), 0.99 (s, 9 H); ^{13}C NMR δ 213.3, 142.5, 141.5, 132.7, 130.9, 129.9, 129.1, 128.1, 127.3, 127.0, 126.7, 44.3, 41.5, 26.5; MS m/z 252 (M^+).

(1,1′-Biphenyl-2-yl)(4-methylphenyl)acetonitrile (13): ^{1}H NMR δ 7.47−7.49 (m, 1 H), 7.33−7.44 (m, 5 H), 7.24−7.29 (m, 3 H), 7.07 (d, 2 H, J = 8.1 Hz), 6.98 (d, 2 H, J = 8.1 Hz), 5.26 (s, 1 H), 2.29 (s, 3 H); ^{13}C NMR δ 141.6, 139.9, 137.7, 133.9, 133.2, 130.5, 129.5, 129.2, 128.8, 128.6, 128.5, 128.1, 127.8, 127.4, 120.4, 38.6, 21.0; MS m/z 283 (M^+). Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 88.68; H, 5.87; N, 5.25.

Preparation of *trans*-Ph(AcO)Pd(PPh_3)$_2$ (9a). A mixture of *trans*-Ph(I)Pd(PPh_3)$_2$ (83 mg, 0.1 mmol), silver acetate (17 mg, 0.1 mmol), and THF (4 cm^3) was stirred under N_2 at room temperature for 1 h. After addition of THF (4 cm^3), the supernatant was separated and then dried under vacuum. A gray solid was obtained (76 mg, 99%). A trace of the starting complex was also present and was not separated: ^{1}H NMR (THF-d_8) δ 7.43−7.44 (m, 12 H), 7.32 (t, 6 H, J = 7.4 Hz), 7.23 (t, 12 H, J = 7.4 Hz), 6.55 (d, 2 H, J = 7.5 Hz), 6.48 (t, 1 H, J = 7.5 Hz), 6.25 (t, 2 H, J = 7.5 Hz), 0.79 (s, 3 H);[17] ^{31}P NMR (THF-d_8) δ 19.1.

Preparation of *trans*-Ph(*p*-MeC_6H_4O)Pd(PPh_3)$_2$ (9b). A mixture of **9a** (38 mg, 0.05 mmol), sodium *p*-cresolate (7 mg, 0.05 mmol), and THF (4 cm^3) was stirred under N_2 at room temperature for 1 h. After addition of THF (1 cm^3), the suspension was filtered to remove a white solid. The solvent was removed under vacuum to give a yellow powder. Recrystallization from toluene/hexane gave yellow microcrystals (21 mg, 52%). A small amount of **9a** was also present and was not separated (**9a**:**9b** = 1:9): ^{1}H NMR (THF-d_8) δ 7.43−7.48 (m, 12 H), 7.26 (t, 6H, J = 7.4 Hz), 7.14 (t, 12 H, J = 7.4 Hz), 6.71 (dd, 2 H, J = 1.4, 7.9 Hz), 6.36 (t, 1 H, J = 7.3 Hz), 6.21−6.27 (m, 4 H), 6.10 (d, 2 H, J = 6.5 Hz), 1.93 (s, 3 H); ^{31}P NMR (THF-d_8) δ 15.5.

Stoichiometric Reaction of *trans*-Ph(X)Pd(PPh_3)$_2$ (9) with Acetophenone. A mixture of **9** (0.01 mmol), acetophenone (12 mg, 0.1 mmol), and THF-d_8 (0.7 cm^3) was heated under N_2 (1 atm) at 50 or 80 °C for 18−21 days. The time course of the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy.

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