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Amido Pincer Complexes of Palladium: Synthesis, Structure, and Catalytic Heck Reaction

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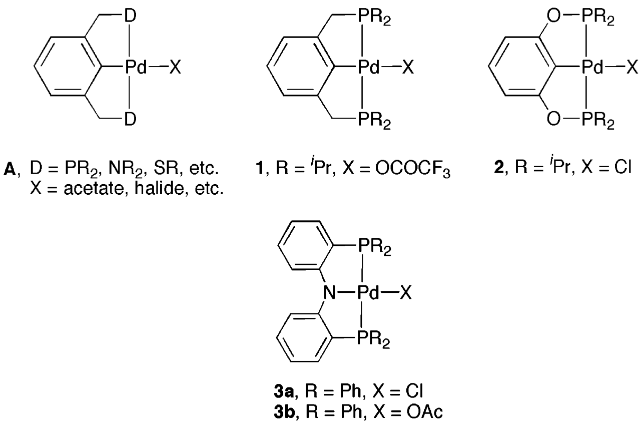
Summary: Palladium complexes containing an o-phenylene-derived amido diphosphine ligand efficiently catalyze the Heck olefination of a wide array of aryl halides, leading to extremely high turnover numbers of up to 4.5×10^7.

Introduction

Palladium-catalyzed aryl olefination, generally referred to as the Heck reaction, is an important method for the formation of carbon−carbon bonds.[1−4] Among the catalysts reported to date, the palladium pincer complexes **A** (Figure 1)[5] constitute an intriguing class of compounds, as they seem to possess a unique balance of reactivity and stability which can be carefully tailored by systematic ligand modifications with multiple choices of donor atoms and substituents thereon. Remarkable examples such as **1**,[6] pioneered by Milstein and coworkers, exhibit extremely high catalytic activity for the Heck reactions with aryl iodides and bromides. While **1** is found to be almost inactive with aryl chlorides, the oxygen-incorporated PCP pincer complex **2** is an efficient catalyst for the functionalization of these industrially important substrates.[7] The distinct reactivity of **2** as compared to **1** is attributed to electronic factors. The high thermal stability of these pincer complexes is believed to be one of the keys to the success of these processes. We envisioned that electronic modification of the palladium PCP pincer complexes with a monoanionic amido diphosphine ligand such as that illustrated in **3** would also lead to catalytically active species for the Heck coupling reactions. We have recently prepared a series of nickel(II) complexes of bis(2-(diphenylphosphino)phenyl)amide ($[PNP]^-$)[8,9] that are remarkably thermally stable. The palladium analogues **3** are thus anticipated to possess appreciably high thermal stability, thereby promising the catalytic activity for the Heck reactions. Herein we present our preliminary results in this endeavor.[10] A report appeared very recently concerning the Heck reaction of ethyl acrylate by palladium complexes supported by a similar amido diphosphine ligand that contains isopropyl substituents at the phosphorus donors.[11]



A, D = PR_2, NR_2, SR, etc.
X = acetate, halide, etc.

1, R = ^{i}Pr, X = $OCOCF_3$

2, R = ^{i}Pr, X = Cl

3a, R = Ph, X = Cl
3b, R = Ph, X = OAc

Figure 1. Representative examples of palladium pincer complexes.

Results and Discussion

The metathetical reaction of $[PNP]Li(THF)_2$[8] with $PdCl_2(PhCN)_2$ in THF at −35 °C produced [PNP]PdCl (**3a**) quantitatively, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. The analogous reaction with $Pd(OAc)_2$ afforded [PNP]Pd(OAc) (**3b**) cleanly. Compounds **3a** and **3b** can be readily isolated as brick red solids in high yield. Both compounds are not sensitive to oxygen and moisture and can be conveniently manipulated in the air for subsequent reactions.

The solution NMR data of these molecules are all consistent with a square-planar geometry, reminiscent of the nickel chemistry.[8] The amido pincer ligand is in a meridional coordination mode, as evidenced by the presence of virtual triplet resonances observed for the *o*-phenylene carbon atoms in the $^{13}C\{^1H\}$ NMR spectra. Single crystals of **3a** suitable for X-ray crystallography were grown from a concentrated benzene solution at

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10.1021/om049888g CCC: $27.50

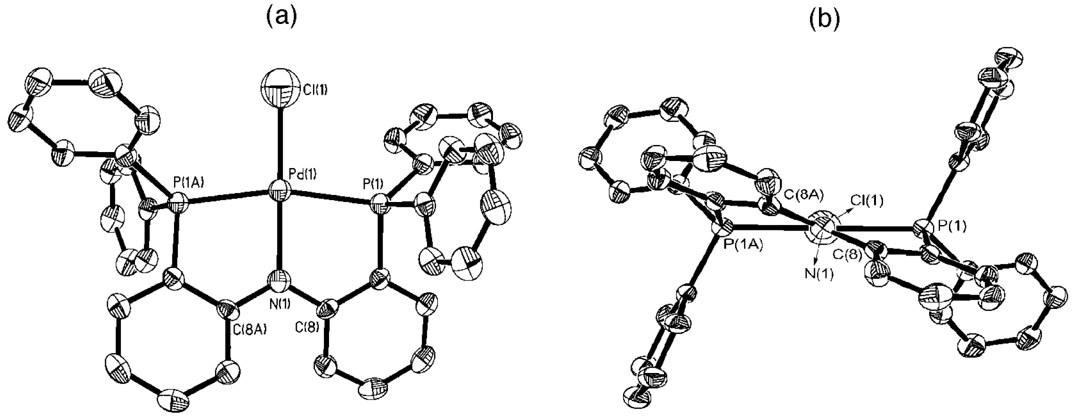

Figure 2. Two views of the molecular structure of [PNP]PdCl (**3a**). Selected bond distances (Å) and angles (deg): Pd(1)−N(1) = 2.056(11), Pd(1)−P(1) = 2.3010(18), Pd(1)−Cl(1) = 2.313(5); N(1)−Pd(1)−P(1) = 82.63(6), P(1A)−Pd(1)−P(1) = 165.27(11), N(1)−Pd(1)−Cl(1) = 180.0000(10), P(1)−Pd(1)−Cl(1) = 97.37(6), C(8)−N(1)−C(8A) = 125.2(10), C(8)−N(1)−Pd(1) = 117.4(5).

room temperature. Figure 2 depicts the solid-state structure of **3a**, in which the four-coordinate palladium atom lies perfectly on the square plane defined by Cl(1), N(1), P(1), and P(1A). Notably, the nitrogen and chlorine atoms are mutually trans to each other (N(1)−Pd(1)−Cl(1) = 180°). The P(1A)−Pd(1)−P(1) angle of 165.27(11)° is smaller than that found in the silyl-derived $PdCl[N(SiMe_2CH_2PPh_2)_2]$ (177.11(2)°)[12] but comparable to those of the PCP pincer complexes such as **2** (160.380(6)°),[13] $PdCl[C_6H_3(CH_2PPh_2)_2\text{-}2,6]$ (162.01(1)°),[14] and $PdCl[C_6H_3(CH_2P^tBu_2)_2\text{-}2,6]$ (165.79(2)°).[15] The two phenylene rings of the backbone were tilted with respect to the coordination plane due to the steric repulsion between the two CH groups ortho to the amido nitrogen atom. The dihedral angle defined by the two phenylene planes is 36.9°. The sum of the angles about N(1) equals 360°, indicating a planar amido nitrogen atom. The angle between the mean coordination plane and the C(8)−N(1)−C(8A) plane is 24° (Figure 2b). The remaining parameters are unexceptional.

As expected, compounds **3a** and **3b** are both thermally stable at elevated temperatures. For instance, no decomposition was observed for **3a** (5.90 mM in *N*-methylpyrrolidone (NMP)) after prolonged heating at 200 °C for >100 h, as indicated by the $^{31}P\{^1H\}$ NMR spectrum. We chose to examine the coupling of bromobenzene with styrene for the survey of the reaction parameters. Specifically, four bases and three solvents were attempted under conditions where they were compatible. As summarized in Table 1, the reaction conditions involving NMP and amines (entries 1 and 2) appear to be superior to the others. It is important to note that no stilbene formation is observed when the reaction is performed in the absence of **3**. The coupling reactions may also be conducted under aerobic conditions or in the presence of a significant amount of water (1:1 with respect to the volume of the solvent employed), although much lower turnover numbers result.

Table 1. Effect of Base and Solvent on the Heck Coupling of Bromobenzene with Styrene[a]

$$\text{PhBr} + \text{Styrene} \xrightarrow[\substack{\text{base, solvent} \\ 110\ ^\circ\text{C, 60 h}}]{1.0\ \text{mol\%}\ \mathbf{3a}} \text{Stilbene}$$

entry	base[b]	solvent[c]	yield (%)[d]
1	$MeNCy_2$	NMP	28
2	NEt_3	NMP	36
3	Cs_2CO_3	NMP	23
4	$MeNCy_2$	dioxane	12
5	NEt_3	dioxane	0
6	Cs_2CO_3	dioxane	20
7	NaO^tBu	dioxane	21
8	$MeNCy_2$	toluene	18
9	NEt_3	toluene	0
10	Cs_2CO_3	toluene	16
11	NaO^tBu	toluene	1

[a] Reaction conditions: 1.0 equiv of PhBr, 1.1 equiv of styrene, 1.0 mol % of **3a**, 1.1 equiv of base, 2 mL of solvent. [b] $MeNCy_2$ = *N*-methyldicyclohexylamine. [c] NMP = *N*-methylpyrrolidone. [d] Determined by GC, based on bromobenzene; average of two runs.

The scope of the Heck coupling with respect to the aryl halide component was investigated (Table 2). Following the lead of Table 1, we attempted to react a variety of aryl iodides, bromides, and chlorides with styrene in NMP at 160 °C in the presence of $MeNCy_2$ as the base. Extraordinarily high turnover numbers of up to 4.5×10^7 (entry 5) and turnover frequencies of up to 1.1×10^6 (per hour, entry 5) are realized for the coupling of iodobenzene with styrene. Not surprisingly, the reactivity follows the order iodide > bromide > chloride. Both ortho- and para-substituted aryl halides can be coupled, although a slower rate is found for the former. As illustrated in Table 2, a number of functional groups are compatible with these catalytic conditions. The catalytic activity of **3b** appears to be as efficient as that of **3a**. No palladium black was observed in all attempts.

The mechanistic possibilities involving a Pd^0/Pd^{II} or Pd^{II}/Pd^{IV} cycle for the Heck reactions in some catalytic systems are currently under debate.[6,16] A competitive experiment involving activated, unactivated, and deactivated aryl bromides (92 mM for each) with styrene catalyzed by **3a** (0.92 mM) in NMP at 160 °C leads to a

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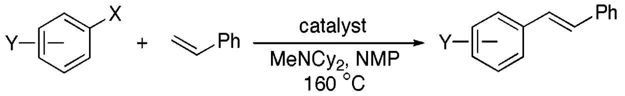
Table 2. Catalytic Heck Reactions of Aryl Halides with Styrene[a]



entry	cat. (amt (mol %))	ArX	*t* (h)	TON	yield (%)[b]
1	**3a** (0.2)	PhI	4	500	100
2	**3a** (0.002)	PhI	39	49 726	99
3	**3a** (0.0002)	PhI	39	500 000	100
4	**3a** (0.00002)	PhI	39	5 000 000	100
5	**3a** (0.000002)	PhI	39	45 505 000	91
6	**3a** (0.2)	4-$BrC_6H_4NO_2$	12	500	100 (90)
7	**3b** (0.2)	4-$BrC_6H_4NO_2$	12	490	98
8	**3a** (0.2)	4-BrC_6H_4CHO	12	500	100 (90)
9	**3b** (0.2)	4-BrC_6H_4CHO	12	500	100
10	**3a** (0.2)	2-BrC_6H_4CHO	39	480	96
11	**3a** (0.2)	4-$BrC_6H_4C(O)Me$	12	500	100 (84)
12	**3a** (0.002)	4-$BrC_6H_4C(O)Me$	110	33,645	67
13	**3b** (0.2)	4-$BrC_6H_4C(O)Me$	12	500	100
14	**3a** (0.2)	2-$BrC_6H_4C(O)Me$	110	375	75
15	**3a** (0.2)	PhBr	110	475	95
16	**3b** (0.2)	PhBr	110	400	80
17	**3a** (0.2)	2-BrC_6H_4F	110	295	59
18	**3a** (0.2)	4-BrC_6H_4OMe	39	125	25
19	**3b** (0.2)	4-BrC_6H_4OMe	110	260	52
20	**3a** (0.2)	4-$BrC_6H_4NMe_2$	39	60	12
21	**3b** (0.2)	4-$BrC_6H_4NMe_2$	39	60	12
22	**3a** (0.2)	4-$ClC_6H_4NO_2$	12	85	17
23	**3a** (0.2)	4-ClC_6H_4CHO	12	50	10
24	**3a** (0.2)	4-$ClC_6H_4C(O)Me$	12	90	18

[a] Reaction conditions: 1.0 equiv of aryl halide, 1.1 equiv of styrene, 1.1 equiv of $MeNCy_2$, 2 mL of NMP. [b] Determined by GC, based on aryl halides; average of two runs. Yields in parentheses refer to isolated yields; average of two runs.

Hammett plot with a reaction constant ρ of 0.6034 (Figure S1). On the basis of this result, it is likely that the rate-determining step in our process is not the oxidative addition of the aryl–halide bond to the metal center of the active species, which would lead instead to a much larger value of reaction constants: e.g., $\rho = 5.2$ for Pd^0 supported by a 1,3-bis(diisopropylphosphino)propane ligand.[17] Similar observations were also reported for systems involving **1** ($\rho = 1.39$)[6] and related compounds,[6,18] in which slow olefin coordination or insertion was suggested.

In summary, we have demonstrated that amido pincer complexes of palladium are highly effective catalysts for Heck coupling reactions. The activities observed for the coupling with iodoarenes are among the highest reported. Further studies involving variation of the palladium amido pincer complexes and mechanism of this catalytic process are currently underway.

Experimental Section

General Procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and were purified by standard methods. The compound $[PNP]Li(THF)_2$ was prepared by following the procedures reported previously.[8] All other chemicals were used as received from commercial vendors. The NMR spectra were recorded on Varian instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane, and coupling constants (J) are in hertz. ^1H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6 and δ 7.27 for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C_6D_6 and δ 77.23 for $CDCl_3$. The assignment of the carbon atoms for all compounds is based on DEPT ^{13}C NMR spectroscopy. ^{31}P NMR spectra are referenced externally using 85% H_3PO_4 at δ 0. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents. Mass spectra were recorded on a Finnigan MAT 95XL mass spectrometer. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer. The Heck coupling reactions were analyzed by GC on a Varian Chrompack CP-3800 instrument equipped with a CP-Sil 5 CB Chrompack capillary column and the yields calculated versus aryl halides or dodecane as an internal standard. The identity of the products was confirmed by comparison with authentic samples.

X-ray Crystallography. Data for [PNP]PdCl (**3a**) were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 using maXus. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions.

Synthesis of [PNP]PdCl (3a). Solid $PdCl_2(PhCN)_2$ (100 mg, 0.261 mmol) was dissolved in THF (4 mL) and cooled to −35 °C. To this was added dropwise a cold THF solution (4 mL) of $[PNP]Li(THF)_2$ (180 mg, 0.267 mmol) at −35 °C. The reaction mixture was stirred at room temperature for 1 h and evaporated to dryness under reduced pressure. The residue was triturated with pentane (9 mL), extracted with CH_2Cl_2 (10 mL), and filtered through a pad of Celite. Solvent was removed in vacuo. The residue was washed with pentane (15 mL) and dried in vacuo to yield the product as a brick red solid; yield 149 mg (84%). Single crystals suitable for X-ray crystallography were grown from a concentrated benzene solution at room temperature. ^1H NMR (C_6D_6, 500 MHz): δ 7.86 (m, 8, Ar), 7.78 (d, 2, Ar), 7.06 (m, 2, Ar), 6.93–6.99 (m, 10, Ar), 6.88 (t, 2, Ar), 6.63 (t, 2, Ar), 6.40 (t, 2, Ar). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 29.79. $^{31}P\{^1H\}$ NMR (THF, 80.95 MHz): δ 29.36. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 163.18 (t, J_{CP} =

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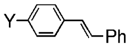
12.70, C), 136.15 (s, CH), 134.51 (t, J_{CP} = 6.79, CH), 132.52 (s, CH), 132.33 (t, J_{CP} = 5.40, C), 131.15 (t, J_{CP} = 11.82, CH), 129.33 (t, J_{CP} = 5.47, CH), 122.23 (t, J_{CP} = 23.19, C), 119.03 (br s, CH), 117.65 (t, J_{CP} = 6.85, CH). Anal. Calcd for $C_{36}H_{28}ClNPdP_2$: C, 63.73; H, 4.16; N, 2.06. Found: C, 63.14; H, 4.36; N, 2.10.

Synthesis of [PNP]Pd(OAc) (3b). Solid $Pd(OAc)_2$ (50 mg, 0.223 mmol) was dissolved in THF (4 mL) and cooled to −35 °C. To this was added dropwise a cold THF solution (4 mL) of $[PNP]Li(THF)_2$ (153 mg, 0.223 mmol) at −35 °C. The reaction mixture was stirred at room temperature for 1 h and evaporated to dryness under reduced pressure. The residue was triturated with pentane (9 mL), extracted with CH_2Cl_2 (10 mL), and filtered through a pad of Celite. Solvent was removed in vacuo. The residue was washed with pentane (15 mL) and dried in vacuo to yield the product as a brick red solid; yield 114 mg (73%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.97 (m, 8, Ar), 7.66 (d, 2, Ar), 6.99−7.08 (m, 14, Ar), 6.83 (t, 2, Ar), 6.38 (t, 2, Ar), 1.93 (s, 3, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.31 MHz): δ 29.12. $^{31}P\{^1H\}$ NMR (THF, 80.95 MHz): δ 28.63. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.70 MHz): δ 175.43 (s, C═O), 162.89 (t, J_{CP} = 12.26, C), 135.26 (s, CH), 134.58 (t, J_{CP} = 7.29, CH), 132.38 (s, CH), 131.60 (t, J_{CP} = 24.51, C), 131.09 (s, CH), 129.26 (t, J_{CP} = 5.41, CH), 123.66 (t, J_{CP} = 23.13, C), 118.80 (br s, CH), 117.74 (t, J_{CP} = 5.91, CH), 23.24 (s, CH_3). Anal. Calcd for $C_{38}H_{31}NO_2PdP_2$: C, 65.01; H, 4.45; N, 2.00. Found: C, 63.77; H, 4.77; N, 1.95.

General Procedures for the Heck Reactions Outlined in Table 2. A Schlenk flask was charged with **3a** or **3b** (1.0 mg for each single experiment) along with an appropriate amount of aryl halide (1.0 equiv), styrene (1.1 equiv), $MeNCy_2$ (1.1 equiv), and NMP (2 mL) and a magnetic stir bar. The flask was capped with a stopper and heated in an oil bath at 160 °C with stirring for a specified period of time. After the reaction mixture was cooled to room temperature, hydrochloric acid (1 M, 6 mL) was added and the product was extracted with diethyl ether (15 mL × 3). The aqueous solution was separated from the organic layer. The diethyl ether solution was washed with deionized water (15 mL × 3), dried over $MgSO_4$, and evaporated to dryness under reduced pressure to afford the desired product, which was then washed with hexane (5 mL × 3) or subject to flash column chromatography on silica gel. For experiments with low catalyst loading (entries 2−5), stock solutions of appropriate concentrations were prepared by dissolving 1.0 mg of [PNP]PdCl in appropriate amounts of NMP and used for each independent run.



***trans*-Stilbene (Y = H).**[19] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (d, 4, J_{HH} = 7.5, o-C_6H_5), 7.46 (t, 4, J_{HH} = 7.5, m-C_6H_5), 7.36 (t, 2, J_{HH} = 7.5, p-C_6H_5), 7.22 (s, 2, CH═CH). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 137.26 (*ipso*-C_6H_5), 128.64 (CH═CH), 128.63 (m-C_6H_5), 127.56 (p-C_6H_5), 126.47 (o-C_6H_5). LRMS (EI): calcd for $C_{14}H_{12}$ m/z 180, found m/z 180.

4-Acetylstilbene (Y = C(O)Me).[19] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93 (d, 2, o-C_6H_4C(O)Me, J_{HH} = 8), 7.54 (d, 2, J_{HH} = 8), 7.52 (d, 2, J_{HH} = 8), 7.37 (t, 2, m-C_6H_5, J_{HH} = 7.5), 7.30 (t, 1, p-C_6H_5, J_{HH} = 7), 7.19 (d, 1, CH═CH, $^3J_{HH}$ = 16.5), 7.09 (d, 1, CH═CH, $^3J_{HH}$ = 16.5), 2.57 (s, 3, Me). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 197.18 (C═O), 141.70 (C), 136.43 (C), 135.66 (C), 131.17 (CH), 128.63 (CH), 128.58 (CH), 128.10 (CH), 127.16 (CH), 126.63 (CH), 126.27 (CH), 26.33 (CH_3). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.12; H, 6.40.

4-Nitrostilbene (Y = NO_2).[19] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.21 (d, 2, o-$C_6H_4NO_2$, J_{HH} = 8.5), 7.62 (d, 2, m-$C_6H_4NO_2$, J_{HH} = 8.5), 7.56 (d, 2, o-C_6H_5CH═CH, J_{HH} = 7.5), 7.41 (t, 2, m-C_6H_5CH═CH, J_{HH} = 7.5), 7.35 (t, 1, p-C_6H_5CH═CH, J_{HH} = 7), 7.27 (d, 1, CH═CH, $^3J_{HH}$ = 16), 7.14 (d, 1, CH═CH, $^3J_{HH}$ = 16). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 146.65 (CNO_2), 143.76 (C), 136.09 (C), 133.21 (CH), 128.82 (CH), 128.77 (CH), 126.95 (CH), 126.77 (CH), 126.18 (CH), 124.05 (CH). LRMS (EI): calcd for $C_{14}H_{11}NO_2$ m/z 225, found m/z 225. Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.35; H, 4.98; N, 6.16.

4-Stilbenecarboxaldehyde (Y = CHO).[19] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.98 (s, 1, CHO), 7.86 (d, 2, o-C_6H_4CHO, J_{HH} = 8.5), 7.63 (d, 2, m-C_6H_4CHO, J_{HH} = 8.5), 7.54 (d, 2, o-C_6H_5CH═CH, J_{HH} = 7.5), 7.39 (t, 2, m-C_6H_5CH═CH, J_{HH} = 7.5), 7.32 (t, 1, p-C_6H_5CH═CH, J_{HH} = 7), 7.24 (d, 1, CH═CH, J_{HH} = 16.5), 7.12 (d, 1, CH═CH, J_{HH} = 16.5). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 191.47 (CHO), 143.22 (C), 136.37 (C), 135.14 (C), 132.01 (CH), 130.07 (CH), 128.69 (CH), 128.37 (CH), 127.14 (CH), 126.78 (CH), 126.75 (CH). LRMS (EI): Calcd for $C_{15}H_{12}O$ m/z 208, found m/z 208.

Experimental Details for the Competition Reactions (Figure S1, Supporting Information). A Schlenk flask was charged with **3a** (2.5 mg, 3.68 μmol, 1 mol % with respect to each of the aryl bromides), aryl bromides (0.368 mmol for each), dodecane (63 mg, 0.371 mmol), styrene (215 mg, 2.064 mmol), $MeNCy_2$ (397 mg, 2.032 mmol), NMP (4 mL), and a magnetic stir bar. The flask was capped with a stopper and heated in an oil bath at 160 °C with stirring. An aliquot was taken with a syringe and subject to GC analysis. The yields of each of the stilbene derivatives were calculated on the basis of the relative intensities with dodecane.

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Supporting Information Available: A figure giving the Hammett plot derived from the competitive reactions and an X-ray crystallographic report for [PNP]PdCl (**3a**), including tables of crystal data and structure refinement, etc.; X-ray data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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