Catalytic Suzuki Coupling Reactions by Amido Phosphine Complexes of Palladium

Lan-Chang Liang,* Pin-Shu Chien, and Mei-Hui Huang

Department of Chemistry and Center for Nanoscience & Nanotechnology, National Sun Yat-sen University, Kaohsiung 80424, Taiwan

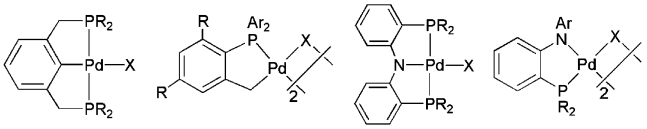
Received October 2, 2004

Treatment of $PdCl_2(PhCN)_2$ with [NP]Li$(THF)_2$ ([NP]$^-$ = *N*-(2-(diphenylphosphino)phenyl)-2,6-diisopropylanilide) in THF affords dimeric {[NP]PdCl}$_2$, which reacts with tricyclohexylphosphine to produce [NP]PdCl(PCy_3). The two phosphorus donors in [NP]PdCl(PCy_3) are mutually cis, as indicated by the solution NMR and X-ray crystallographic studies. Both {[NP]PdCl}$_2$ and [NP]PdCl(PCy_3) are highly active catalyst precursors for Suzuki coupling reactions of a wide array of aryl halides, including those featuring electronically deactivated and sterically hindered characteristics.

Introduction

Palladium-catalyzed cross-coupling reactions are some of the most versatile methods for the formation of carbon−carbon bonds.[1−4] The search for appropriate ancillary ligands that facilitate the generation of highly active catalyst precursors is of current interest. Significant progress has been made recently with the employment of ligands such as electron-rich, sterically hindered phosphines[5−9] and N-heterocyclic carbenes.[10−14] Orthopalladated phosphine complexes constitute an intriguing class of compounds, as catalyst activity and reaction selectivity can be efficiently probed by systematic ligand modifications.[15] Chart 1 depicts representative examples of the phosphine palladacycles **1** and **2**.[16−18] We envisioned that electronic modification of compounds **1** and **2** with a monoanionic amido phosphine ligand such as those illustrated in **3** and **4** would also lead to catalytically active species for cross-coupling reactions. We recently demonstrated that compounds of the type **3** are highly active catalysts for Heck olefination of aryl halides.[19] In a parallel pursuit, we have set out to examine the possibility of **4** for catalytic carbon−carbon bond formation, with the current focus on Suzuki coupling reactions.[20] In this contribution, we describe our results in this regard with the amido phosphine ligand being *N*-(2-(diphenylphosphino)phenyl)-2,6-diisopropylanilide ([NP]$^-$).

Chart 1. Representative Examples of Phosphine Palladacycles



1 2 3 4

Results and Discussion

The metathetical reaction of [NP]Li$(THF)_2$[21] with $PdCl_2(PhCN)_2$ in THF at −35 °C produced diamagnetic, dimeric {[NP]PdCl}$_2$ as a greenish blue solid in quantitative yield. The chloride complex was fully characterized by multinuclear NMR spectroscopy and elemental analysis. Analogous to the nickel chemistry of [NP]$^-$,[22] the isopropylmethyl groups in {[NP]PdCl}$_2$ are diastereotopic, as evidenced by ^{1}H and ^{13}C NMR spectroscopy, implying restricted rotation about the N−Ar bond. Without crystallographic data, we tentatively formulate

* To whom correspondence should be addressed. E-mail: lcliang@mail.nsysu.edu.tw. Fax: +886-7-5253908.

(1) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998.
(2) Miyaura, N. *Top. Curr. Chem.* **2002**, *219*.
(3) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176−4211.
(4) Scrivanti, A.; Beghetto, V.; Matteoli, U.; Antonaroli, S.; Marini, A.; Mandoj, F.; Paolesse, R.; Crociani, B. *Tetrahedron Lett.* **2004**, *45*, 5861−5864.
(5) Littke, A. F.; Dai, C. Y.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020−4028.
(6) Liu, S. Y.; Choi, M. J.; Fu, G. C. *Chem. Commun.* **2001**, 2408−2409.
(7) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722−9723.
(8) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1871−1876.
(9) Yin, J. J.; Rainka, M. P.; Zhang, X. X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162−1163.
(10) Zhang, C. M.; Huang, J. K.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804−3805.
(11) Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93−96.
(12) Weskamp, T.; Bohm, V. P.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *585*, 348−352.
(13) Biakey, S. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2003**, *125*, 6046−6047.
(14) Navarro, O.; Kelly, R. A.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194−16195.
(15) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759−1792.
(16) Beller, M.; Fischer, H.; Herrmann, W. A.; Ofele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848−1849.
(17) Gibson, S.; Foster, D. F.; Eastham, G. R.; Tooze, R. P.; Cole-Hamilton, D. J. *Chem. Commun.* **2001**, 779−780.
(18) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687−11688.
(19) Huang, M.-H.; Liang, L.-C. *Organometallics* **2004**, *23*, 2813−2816.
(20) The catalytic Suzuki couplings mediated by **3** will be reported separately.
(21) Liang, L.-C.; Lee, W.-Y.; Hung, C.-H. *Inorg. Chem.* **2003**, *42*, 5471−5473.
(22) Liang, L.-C.; Lee, W.-Y.; Yin, C.-C. *Organometallics* **2004**, *23*, 3538−3547.

10.1021/om0492395 CCC: $30.25
Publication on Web 12/23/2004

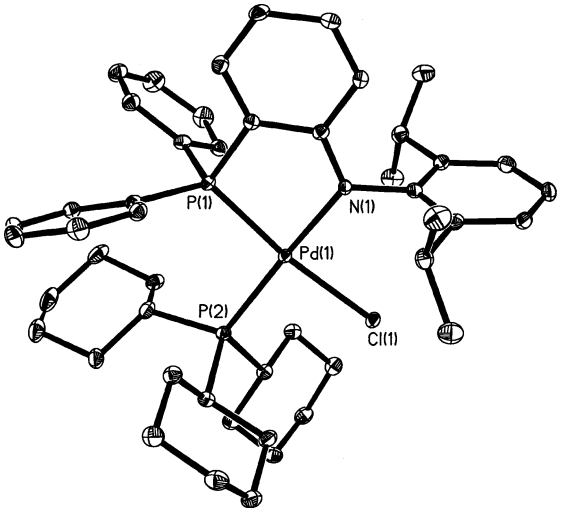
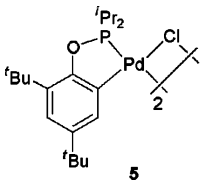


Figure 1. Molecular structure of [NP]PdCl(PCy_3) with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Pd(1)−N(1) = 2.079(2), Pd(1)−P(1) = 2.2532(8), Pd(1)−P(2) = 2.3131(8), Pd(1)−Cl(1) = 2.3565(7); N(1)−Pd(1)−P(1) = 82.09(7), N(1)−Pd(1)−P(2) = 176.26(7), P(1)−Pd(1)−P(2) = 100.04(3), N(1)−Pd(1)−Cl(1) = 89.86(7), P(1)−Pd(1)−Cl(1) = 171.94(3), P(2)−Pd(1)−Cl(1) = 88.01(3).

this compound as a chloride-bridged dimer, presumably in the solid state, on the basis of its facile association with Lewis bases. Addition of PCy_3 to an ethereal solution of {[NP]PdCl}$_2$ generated quantitatively [NP]-PdCl(PCy_3) as a brown crystalline solid. The room-temperature $^{31}P\{^1H\}$ NMR spectrum of [NP]PdCl(PCy_3) exhibits two doublet resonances with equal intensity at 52.20 and 36.19 ppm for $[NP]^-$ and PCy_3, respectively. The coupling constant of 15 Hz is consistent with a cis relationship between the two phosphorus donors. Both {[NP]PdCl}$_2$ and [NP]PdCl(PCy_3) are thermally stable and are not sensitive to air or water. For instance, no decomposition was observed when {[NP]PdCl}$_2$ (5.1 mM in dioxane) or [NP]PdCl(PCy_3) (7.0 mM in dioxane) was heated to 120 °C for >2 days in the presence of water (*2000 equiv*!) under aerobic conditions, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. The unusual stability of these palladium amides toward protonation in the presence of water is remarkable,[23] a result that is ascribable to the association of the phosphorus donor of the $[NP]^-$ ligand to the palladium center.

Single crystals of [NP]PdCl(PCy_3) suitable for X-ray diffraction analysis were grown from a concentrated dioxane solution at room temperature. As depicted in Figure 1, the solid-state structure is consistent with the solution structure observed by NMR spectroscopy. The coordinated PCy_3 is cis to the phosphorus donor of the amido phosphine ligand, with a P−Pd−P angle of 100.04(3)°. The palladium center lies perfectly on the square plane defined by the four donor atoms. The N(1)−Pd(1)−P(1) angle of 82.09(7)° is similar to the corresponding values of five-membered palladacycles



5

such as the phosphinite derivative **5** (80.24(7)°).[24] As expected, the diisopropylphenyl ring is roughly perpendicular to the N−phenylene−P plane with a dihedral angle of 88.6°, thereby providing steric protection for the axial faces of the palladium center.

To survey the reaction parameters for the catalytic Suzuki couplings, we chose to examine four bases ($K_3PO_4 \cdot H_2O$, K_3PO_4, K_2CO_3, and Cs_2CO_3) and two solvents (dioxane and toluene). Heating at elevated temperatures was required, due likely to the generally low solubility of these bases in the solvents that we screened. We found that reactions performed in dioxane with $K_3PO_4 \cdot H_2O$ or K_3PO_4 as the base at 110 °C appear to be superior to the others.[25]

The scope of the Suzuki coupling with respect to the aryl halide component was investigated (Table 1). A number of aryl iodides, bromides, and chlorides have been successfully coupled with arylboronic acids. Specifically, {[NP]PdCl}$_2$ is an effective catalyst precursor for the coupling of activated, unactivated, and deactivated bromides and iodides (entries 1−21). Extremely high turnover numbers of up to 6.8×10^7 (per Pd, entry 19) and turnover frequencies of up to 3.1×10^6 (per Pd per hour, entry 18) are realized for the coupling of electronically deactivated 4-bromoanisole with phenylboronic acid. This condition also allows for the coupling of heterocyclic (entry 5) and 2,6-disubstituted (entries 9−12) substrates. Of particular interest is the formation of tri-ortho-substituted biaryls (entries 11 and 12) at efficient turnover rates, although the palladium catalyst is supported by a sterically demanding amido phosphine ligand.

The coupling of aryl chlorides is also achieved (entries 22−31). Although both {[NP]PdCl}$_2$ and [NP]PdCl-(PCy_3) exhibit comparable activities for the activated substrates (e.g., entry 22 versus entry 25), the latter complex outperforms the former with respect to the unactivated and deactivated substrates (e.g., entry 23 versus entry 27). The higher efficiency of [NP]PdCl-(PCy_3) relative to {[NP]PdCl}$_2$ is attributed to the electronic modification of the coordinated tricyclohexylphosphine.[26] Consistent with the phenomenal stability of these palladium compounds, the coupling reactions can be conducted under aerobic conditions in the presence of water (entry 1). No palladium black was observed in any of the attempts.

To gain insights into the reaction mechanism, competitive experiments involving activated, unactivated, and deactivated aryl bromides with phenylboronic acid in dioxane at 110 °C were performed, leading to Hammett plots with reaction constants ρ of 0.4847 for {[NP]-

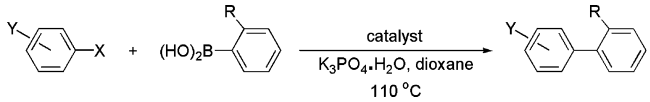
(23) Fryzuk, M. D.; Macneil, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3592−3593.

(24) Bedford, R. B.; Hazelwood, S. L.; Horton, P. N.; Hursthouse, M. B. *Dalton* **2003**, 4164−4174.

(25) Attempted catalysis runs in a water/dioxane mixture at room temperature led to turnover frequencies much lower than those reported in Table 1, due to the formation of bilayers in which the aqueous potassium phosphate monohydrate solution is separated from the dioxane solution that contains the other starting materials. Increasing the reaction temperature of such solutions to 110 °C, however, proved as efficient as those performed in the absence of water.

(26) Controlled experiments showed that the turnover frequencies for the couplings of aryl chlorides catalyzed by [NP]PdCl(PPh_3) are notably lower than those found for [NP]PdCl(PCy_3), suggesting the participation of PCy_3 in the catalytic cycles. Spectroscopic data for [NP]-PdCl(PPh_3): $^{31}P\{^1H\}$ NMR (1,4-dioxane, 80.953 MHz) δ 54.13 (d, $^2J_{PP}$ = 15 Hz, NP), 27.85 (d, $^2J_{PP}$ = 15 Hz, PPh_3).

Table 1. Catalytic Suzuki Reactions of Aryl Halides with Arylboronic Acids[a]



entry	catalyst[b] (amt, mol %)	ArX	R	*t* (h)	TON	yield (%)[c]
1	A (0.05)	4-$BrC_6H_4NO_2$	H	1	1 000	100 (100)[d]
2	A (0.05)	4-$BrC_6H_4C(O)Me$	H	1	1 000	100 (100)
3	A (0.05)	4-BrC_6H_4CHO	H	1	1 000	100
4	A (0.05)	2-BrC_6H_4F	H	1	1 000	100 (94)
5	A (0.05)	2-bromothiophene	H	1	1 000	100
6	A (0.05)	PhBr	H	1	1 000	100
7	A (0.05)	4-BrC_6H_4Me	H	1	1 000	100 (96)
8	A (0.05)	$BrC_6H_3Me_2$-3,5	H	1	1 000	100
9	A (0.05)	$BrC_6H_2Me_3$-2,4,6	H	1	890	89 (89)
10	A (0.05)	$BrC_6H_2{}^iPr_3$-2,4,6	H	12	730	73
11	A (0.05)	$BrC_6H_2Me_3$-2,4,6	Me	24	820	82
12	A (0.05)	$BrC_6H_2{}^iPr_3$-2,4,6	Me	24	340	34
13	A (0.05)	4-BrC_6H_4OMe	H	1	1 000	100 (93)
14	A (0.05)	4-$BrC_6H_4NMe_2$	H	12	980	98 (86)
15	A (0.000 5)	4-BrC_6H_4OMe	H	1	96 000	96
16	A (0.000 05)	4-BrC_6H_4OMe	H	1	350 000	35
17	A (0.000 005)	4-BrC_6H_4OMe	H	12	10 000 000	100
18	A (0.000 000 5)	4-BrC_6H_4OMe	H	12	37 000 000	37
19	A (0.000 000 5)	4-BrC_6H_4OMe	H	24	68 000 000	68
20	A (0.05)	PhI	H	12	1 000	100
21	A (0.05)	4-IC_6H_4OMe	H	12	1 000	100 (99)
22	A (0.05)	4-$ClC_6H_4NO_2$	H	24	840	84
23	A (0.05)	PhCl	H	24	110	11
24	B (0.1)	4-$ClC_6H_4C(O)Me$	H	24	990	99
25	B (0.1)	4-$ClC_6H_4NO_2$	H	24	970	97
26	B (0.1)	4-ClC_6H_4CHO	H	24	950	95
27	B (0.1)	PhCl	H	24	530	53
28	B (0.1)	2-ClC_6H_4Me	H	24	550	55
29	B (0.1)	4-ClC_6H_4Me	H	24	540	54
30	B (0.1)	$ClC_6H_3Me_2$−3,5	H	24	450	45
31	B (0.1)	4-ClC_6H_4OMe	H	24	420	42

[a] Reaction conditions: 1.0 equiv of aryl halide, 1.5 equiv of boronic acids, 2.0 equiv of $K_3PO_4 \cdot H_2O$, 4 mL of 1,4-dioxane. Reaction times have not been minimized. [b] Catalyst A, $\{[NP]PdCl\}_2$; catalyst B, [NP]PdCl(PCy_3). [c] Determined by GC, based on aryl halides; average of two runs. Yields in parentheses refer to isolated yields; average of two runs. [d] Reaction run under aerobic conditions in the presence of 0.5 mL of water.

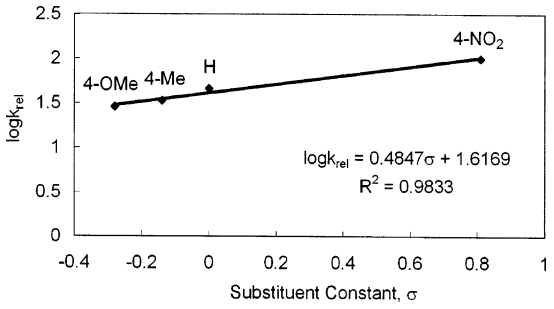


Figure 2. Hammett plot for the coupling of 4-substituted phenyl bromides with phenylboronic acid catalyzed by $\{[NP]PdCl\}_2$ in dioxane at 110 °C, providing the reaction constant $\rho = 0.4847$.

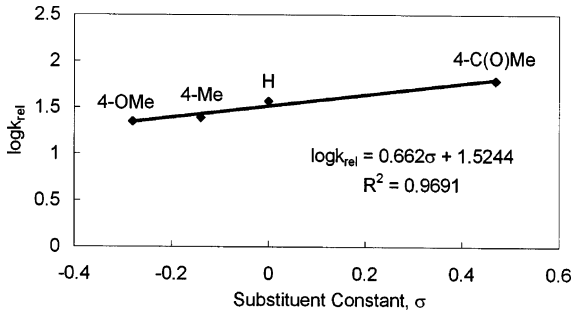


Figure 3. Hammett plot for the coupling of 4-substituted phenyl bromides with phenylboronic acid catalyzed by [NP]-PdCl(PCy_3) in dioxane at 110 °C, providing the reaction constant $\rho = 0.6620$.

$PdCl\}_2$ (Figure 2) and 0.6620 for [NP]PdCl(PCy_3) (Figure 3). The low ρ value likely suggests that aryl halide oxidative addition is not the rate-determining step in this process. This result is consistent with that obtained from the Heck olefination catalyzed by **3**.[19] A much larger value of $\rho = 5.2$ was reported for oxidative addition of aryl halides to Pd^0 supported by a 1,3-bis-(diisopropylphosphino)propane ligand.[27] Similar low ρ values were also reported for other catalytic Suzuki coupling reactions, in which transmetalation was suggested to be slow.[28,29]

Conclusions

In summary, we have demonstrated that the diarylamido phosphine complexes of palladium are highly effective catalysts for Suzuki coupling reactions. It is somewhat surprising that these palladium compounds are air- and water-stable at elevated temperatures, given the inherent reactivity of the palladium−amide bond. A diverse array of aryl halides, including sterically hindered, electronically deactivated, and heterocyclic substrates, have been successfully coupled in this

(27) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665−1673.
(28) Weissman, H.; Milstein, D. *Chem. Commun.* **1999**, 1901−1902.
(29) Zim, D.; Lando, V. R.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2001**, *3*, 3049−3051.

process. Extremely low catalyst loadings for the coupling of 4-bromoanisole are particularly attractive. In view of the ease with which the substituents at the donor atoms in $[NP]^-$ can be readily modified, we anticipate that further enhancements in catalytic activity will be promising. Studies along this line 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 $[NP]Li(THF)_2$[21] was prepared by following the procedures reported previously. 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. ^{1}H 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 and ^{19}F NMR spectra are referenced externally using 85% H_3PO_4 at δ 0 and $CFCl_3$ in $CHCl_3$ at δ 0, respectively. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents. High-resolution mass spectra were recorded on a Bruker Apex mass spectrometer. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer. The Suzuki 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 $[NP]PdCl(PCy_3)$ 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 the WinGX crystallographic software package. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions.

Synthesis of $\{[NP]PdCl\}_2$. 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 a solution of $[NP]Li(THF)_2$ (153 mg, 0.261 mmol) in THF (4 mL) at −35 °C. The reaction mixture was naturally warmed to room temperature with stirring. After being stirred at room temperature for 1 h, the solution was evaporated to dryness under reduced pressure. The solid residue was extracted with CH_2Cl_2 (8 mL) and the extract filtered through a pad of Celite. Solvent was removed in vacuo, and the solid was washed with pentane (5 mL × 2), affording the product as a blue-green solid; yield 148.8 mg (98.7%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.67 (m, 4, Ar), 7.13 (m, 1, Ar), 7.09 (m, 2, Ar), 7.03 (m, 2, Ar), 6.97 (m, 4, Ar), 6.76 (m, 2, Ar), 6.22 (m, 1, Ar), 6.09 (m, 1, Ar), 3.74 (septet, 2, C*H*Me$_2$), 1.29 (d, 6, CH*Me*$_2$), 1.12 (d, 6, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.70 MHz): δ 168.41 (d, J_{CP} = 24.60, C), 147.69 (s, C), 146.60 (s, C), 134.22 (s, CH), 134.00 (d, J_{CP} = 5.52, CH), 133.43 (s, CH), 131.71 (s, CH), 130.56 (d, J_{CP} = 58.99, C), 129.14 (d, J_{CP} = 6.28, CH), 126.70 (s, CH), 124.38 (s, CH), 115.63 (d, J_{CP} = 16.44, CH), 115.01 (d, J_{CP} = 8.16, CH), 109.26 (d, J_{CP} = 61.75, C), 28.92 (s, *C*HMe$_2$), 24.96 (s, CH*Me*$_2$), 24.54 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.31 MHz): δ 57.76. ^{31}P{^{1}H} NMR (THF, 80.95 MHz): δ 53.99. Anal. Calcd for $(C_{30}H_{31}ClNPPd)_2$: C, 62.29; H, 5.40; N, 2.42. Found: C, 62.54; H, 5.47; N, 2.45.

Synthesis of $[NP]PdCl(PCy_3)$. Method 1. A colorless solution of tricyclohexylphosphine (39 mg, 0.14 mmol) in 1,4-dioxane (3 mL) was added to a green solution of $\{[NP]PdCl\}_2$ (81 mg, 0.07 mmol) in 1,4-dioxane (3 mL) at room temperature. The reaction solution was stirred at room temperature for 3 min to give a dark brown solution. The solution was then kept at room temperature for 2 days without stirring to allow for the crystallization of the product. Brown crystals thus obtained were suitable for X-ray diffraction study; yield 90 mg (75%).

Method 2. The reaction may also be conducted in THF solution under conditions similar to those described in method 1. The product was isolated as a brown solid; yield 92%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03 (dd, 4, Ar), 7.56 (m, 2, Ar), 7.50 (m, 4, Ar), 7.14 (s, 3, Ar), 6.75 (t, 1, Ar), 6.60 (dd, 1, Ar), 6.09 (t, 1, Ar), 5.70 (dd, 1, Ar), 3.40 (septet, 2, C*H*Me$_2$), 2.20 (m, 3, Cy), 1.60 (m, 15, Cy), 1.52 (m, 6, Cy), 1.30 (d, 6, CH*Me*$_2$), 1.13 (m, 3, Cy), 0.94 (d, 6, CH*Me*$_2$), 0.89 (m, 6, Cy). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.31 MHz): δ 52.20 (d, $^2J_{PP}$ = 15.38, NP), 36.19 (d, $^2J_{PP}$ = 15.38, PCy_3). ^{31}P{^{1}H} NMR (1,4-dioxane, 80.95 MHz): δ 51.45 (d, $^2J_{PP}$ = 14.65, NP), 36.01 (d, $^2J_{PP}$ = 14.41, PCy_3). ^{31}P{^{1}H} NMR (THF, 80.95 MHz): δ 51.36 (d, $^2J_{PP}$ = 14.65, NP), 35.69 (d, $^2J_{PP}$ = 14.65, PCy_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.70 MHz): δ 164.94 (d, J_{CP} = 25.39, C), 147.36 (s, C), 145.66 (s, C), 134.35 (d, J_{CP} = 11.82, CH), 132.80 (s, CH), 131.95 (s, CH), 131.38 (s, CH), 131.24 (d, J_{CP} = 49.40, C), 128.58 (d, J_{CP} = 10.94, CH), 124.33 (s, CH), 122.61 (s, CH), 114.09 (d, J_{CP} = 14.08, CH), 114.03 (d, J_{CP} = 57.19, C), 112.13 (d, J_{CP} = 8.67, CH), 34.89 (d, $^1J_{CP}$ = 21.37, PCH), 29.82 (s, CH_2), 28.08 (s, *C*HMe$_2$), 27.16 (d, $^2J_{CP}$ = 10.94, CH_2), 26.18 (s, CH_2), 24.40 (s, CH*Me*$_2$), 23.74 (s, CH*Me*$_2$). Anal. Calcd for $C_{48}H_{64}ClNP_2Pd$-(dioxane)$_{0.5}$: C, 66.51; H, 7.59; N, 1.55. Found: C, 66.17; H, 7.65; N, 1.48.

General Procedures for the Suzuki Reactions Outlined in Table 1. A Schlenk flask was sequentially charged with the palladium catalyst $\{[NP]PdCl\}_2$ or $[NP]PdCl(PCy_3)$ (1.0 mg for each single experiment), aryl halide (1.0 equiv), arylboronic acid (1.5 equiv), potassium phosphate monohydrate (2.0 equiv), 1,4-dioxane (4 mL), and a magnetic stir bar. The flask was capped with a glass stopper and heated in an oil bath at 110 °C with stirring for a specified period of time. After being cooled to room temperature, the reaction mixture was diluted with diethyl ether (8 mL), filtered through a pad of Celite, and treated with aqueous NaOH solution (3 mL, 1 M). The diethyl ether solution was separated from the aqueous layer, dried over $MgSO_4$, and evaporated to dryness under reduced pressure to afford the desired product. For experiments with low catalyst loading (entries 15−19), stock solutions of appropriate concentrations were prepared by dissolving 1.0 mg of the palladium catalyst in appropriate amounts of dioxane and used for each independent run.

Biphenyl.[30] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.74 (d, 4, J = 8.0 Hz, ortho), 7.57 (t, 4, J = 6.9 Hz, meta), 7.48 (t, 2, J = 7 Hz, para). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 141.17 (ipso), 128.71 (CH), 127.20 (CH, para), 127.11 (CH). HRMS (EI): calcd for $C_{12}H_{10}$ *m/z* 154.0783, found *m/z* 154.0779.

4-(Dimethylamino)biphenyl.[31] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (d, 2, J = 7.8 Hz, ortho C_6H_5), 7.57 (d, 2, J = 8.5 Hz), 7.45 (t, 2, J = 7.8 Hz, meta C_6H_5), 7.31 (t, 1, J = 7.5 Hz, para C_6H_5), 6.86 (d, 2, J = 8.5 Hz), 3.04 (s, 6, NMe_2). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 149.91, 141.17, 129.25, 128.61 (CH), 127.66 (CH), 126.25 (CH), 125.96 (para C_6H_5), 112.78 (CH), 40.56 (NMe_2). HRMS (EI): calcd for $C_{14}H_{15}N$ *m/z* 197.1204, found *m/z* 197.1201.

4-Acetylbiphenyl.[31] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.04 (d, 2, J = 8.5 Hz), 7.69 (d, 2, J = 8.5 Hz), 7.64 (d, 2, J = 7.5 Hz, ortho C_6H_5), 7.48 (t, 2, J = 7.5 Hz, meta C_6H_5), 7.41 (t, 1, J = 7.3 Hz, para C_6H_5), 2.64 (s, 3, CH_3). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 197.65 (C=O), 145.65, 139.75, 135.74, 128.87 (CH), 128.83 (CH), 128.15 (para C_6H_5), 127.17 (CH), 127.11

(30) Li, G. Y. *J. Organomet. Chem.* **2003**, *653*, 63−68.
(31) Najera, C.; Gil-Moltó, J.; Karlström, S.; Falvello, L. R. *Org. Lett.* **2003**, *5*, 1451−1454.

(CH), 26.56 (CH_3). HRMS (EI): calcd for $C_{14}H_{12}O$ *m/z* 196.0888, found *m/z* 196.0885.

4-Methoxybiphenyl.[7] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61 (d, 2, J = 8.5 Hz), 7.59 (d, 2, J = 8.5 Hz), 7.47 (t, 2, J = 7.8 Hz, meta C_6H_5), 7.36 (t, 1, J = 7.5 Hz, para C_6H_5), 7.03 (d, 2, J = 8.5 Hz), 3.89 (s, 3, CH_3). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 159.10, 140.77, 133.72, 128.68 (CH), 128.10 (CH), 126.69 (CH), 126.61 (para C_6H_5), 114.16 (CH), 55.27 (CH_3). HRMS (EI): calcd for $C_{13}H_{12}O$ *m/z* 184.0888, found *m/z* 184.0884.

4-Methylbiphenyl.[32] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.79 (d, 2, J = 8.3 Hz), 7.70 (d, 2, J = 8.0 Hz), 7.62 (t, 2, J = 6.8 Hz, meta C_6H_5), 7.52 (t, 1, J = 7.5 Hz, para C_6H_5), 7.44 (d, 2, J = 8.0 Hz), 2.59 (s, 3, CH_3). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 141.08, 138.28, 136.88, 129.43 (CH), 128.65 (CH), 126.92 (CH), 126.89 (CH), 21.02 (CH_3). HRMS (EI): calcd for $C_{13}H_{12}$ *m/z* 168.0939, found *m/z* 168.0936.

4-Nitrobiphenyl.[33] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.28 (d, 2, J = 9.0 Hz), 7.72 (d, 2, J = 9.0 Hz), 7.32 (d, 2, J = 7.8 Hz), 7.52 (t, 2, J = 7.3 Hz, meta C_6H_5), 7.46 (t, 1, J = 6.5 Hz, para C_6H_5).^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 147.46, 146.87, 138.55, 129.04 (CH), 128.83 (para C_6H_5), 127.62 (CH), 127.24 (CH), 123.96 (CH). HRMS (EI): calcd for $C_{12}H_9NO_2$ *m/z* 199.0633, found *m/z* 199.0630.

2,4,6-Triisopropylbiphenyl.[34] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51 (t, 2, J = 7.5 Hz, meta C_6H_5), 7.46 (t, 1, J = 7.3 Hz, para C_6H_5), 7.33 (d, 2, J = 8.5 Hz, ortho C_6H_5), 7.22 (s, 2, meta $C_6H_2{}^iPr_3$), 3.10 (septet, 1, J = 7.0 Hz, para C*H*Me_2), 2.77 (septet, 2, J = 7.0 Hz, ortho C*H*Me_2), 1.46 (d, 6, J = 7.0 Hz, para CH*Me*$_2$), 1.23 (d, 12, J = 7.0 Hz, ortho CH*Me*$_2$). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 147.82, 146.51 (ortho $C_6H_2{}^iPr_3$), 140.88, 137.11, 129.80 (CH), 127.89 (CH), 126.40 (para C_6H_5), 120.49 (CH), 34.30 (para *C*HMe$_2$), 30.26 (ortho *C*HMe$_2$), 24.23 (ortho-CH*Me*$_2$), 24.12 (para CH*Me*$_2$). HRMS (EI): calcd for $C_{21}H_{28}$ *m/z* 280.2191, found *m/z* 280.2189.

2,4,6-Trimethylbiphenyl.[35] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (t, 2, J = 7.5 Hz, meta C_6H_5), 7.50 (t, 1, J = 7.5 Hz, para C_6H_5), 7.33 (d, 2, J = 7.5 Hz, ortho C_6H_5), 7.14 (s, 2, meta $C_6H_2Me_3$), 2.52 (s, 3, para $C_6H_2Me_3$), 2.21 (s, 6, ortho $C_6H_2Me_3$). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 141.07, 139.03, 136.45, 135.87 (ortho $C_6H_2Me_3$), 129.24 (CH), 128.32 (CH), 128.02 (CH), 126.45 (para C_6H_5), 20.98 (para Me), 20.70 (ortho Me). HRMS (EI): calcd for $C_{15}H_{16}$ *m/z* 196.1252, found *m/z* 196.1249.

2-Fluorobiphenyl.[36] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.63 (d, 2, J = 7.3 Hz), 7.52 (m, 3), 7.44 (t, 1, J = 7.4 Hz), 7.37 (m, 1), 7.27 (t, 1, J = 7.4 Hz), 7.22 (t, 1, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 159.74 (J_{CF} = 248 Hz, CF), 135.79 (ipso C_6H_5), 130.74 (J_{CF} = 3 Hz, CH), 129.01 (J_{CF} = 3 Hz, ortho C_6H_5), 128.92 (J_{CF} = 8 Hz, CH), 128.40 (meta C_6H_5), 127.92 (J_{CF} = 200 Hz, ipso C_6H_4F), 127.62 (para C_6H_5), 124.30 (J_{CF} = 4 Hz, CH), 116.05 (J_{CF} = 23 Hz, CH). ^{19}F NMR ($CDCl_3$, 188.15 MHz): δ −119.38. HRMS (EI): calcd for $C_{12}H_9F$ *m/z* 172.0688, found *m/z* 172.0685.

2-Phenylthiophene.[37] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (d, 2, J = 7.0 Hz, ortho C_6H_5), 7.47 (t, 2, J = 7.5 Hz, meta C_6H_5), 7.41 (dd, 1, J = 3.5 Hz, J = 1.0 Hz), 7.381 (t, 1, J = 7.5 Hz, para C_6H_5), 7.35 (dd, 1, J = 5.0 Hz, J = 1.0 Hz), 7.17 (dd, 1, J = 5.0 Hz, J = 3.5 Hz). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 144.35, 134.33, 128.82 (CH), 127.94 (CH), 127.38 (CH), 125.88 (CH), 124.73 (CH), 123.01 (CH). HRMS (EI): calcd for $C_{10}H_8S$ *m/z* 160.0347, found *m/z* 160.0341.

4-Phenylbenzaldehyde.[38] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.05 (s, 1, CH=O), 7.95 (d, 2, J = 8.0 Hz), 7.74 (d, 2, J = 8.0 Hz), 7.64 (d, 2, J = 7.5 Hz), 7.49 (t, 2, J = 7.6 Hz, meta C_6H_5), 7.43 (t, 1, J = 7.5 Hz, para C_6H_5). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 191.78 (C=O), 146.96, 139.49, 135.02, 130.11 (CH), 128.87 (CH), 128.34 (para C_6H_5), 127.49 (CH), 127.19 (CH). HRMS (EI): calcd for $C_{13}H_{10}O$ *m/z* 182.0732, found *m/z* 182.0727.

3,5-Dimethylbiphenyl.[39] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.89 (d, 2, J = 8.3 Hz, ortho C_6H_5), 7.71 (t, 2, J = 7.8 Hz, meta C_6H_5), 7.62 (t, 1, para C_6H_5), 7.54 (s, 2, ortho $C_6H_3Me_2$), 7.29 (s, 1, para $C_6H_3Me_2$), 2.68 (s, 6, $C_6H_3Me_2$). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 141.41, 141.19, 138.07, 128.83 (CH), 128.56 (CH), 127.09 (CH), 126.98 (CH), 125.04 (CH), 21.30 (Me). HRMS (EI): calcd for $C_{14}H_{14}$ *m/z* 182.1096, found *m/z* 182.1092.

Representative Example of Experimental Details for the Competition Reactions. A Schlenk flask was charged with [NP]PdCl(PCy_3) (1.0 mg, 1.16 μmol, 0.4 mol % with respect to each of the aryl bromides), aryl bromides (0.291 mmol for each), phenylboronic acid (1.16 mmol), potassium phosphate monohydrate (2.33 mmol), 1,4-dioxane (4 mL), and a magnetic stir bar. The flask was capped with a glass stopper and heated in an oil bath at 110 °C with stirring for 15 min. An aliquot was taken with a syringe and subjected to GC analysis. Yields were calculated versus aryl halides or dodecane as an internal standard. The Hammett plots are shown in Figures 2 and 3.

Acknowledgment. We thank the National Science Council of Taiwan for financial support (Grant No. NSC 93-2113-M-110-016) of this work and Mr. Ting-Shen Kuo at the Instrumentation Center of National Taiwan Normal University for solving the X-ray structure of [NP]PdCl(PCy_3).

Supporting Information Available: Tables and figures giving the X-ray crystallographic report and data in CIF format for [NP]PdCl(PCy_3). This material is available free of charge via the Internet at http://pubs.acs.org.

OM0492395

(32) Mowery, M. E.; DeShong, P. *J. Org. Chem.* **1999**, *64*, 3266−3270.
(33) Mori, Y.; Seki, M. *J. Org. Chem.* **2003**, *68*, 1571−1574.
(34) Hartmann, N.; Niemeyer, M. *Synth. Commun.* **2001**, *31*, 3839−3846.
(35) Anderson, J. C.; Namli, H.; Roberts, C. A. *Tetrahedron* **1997**, *53*, 15123−15134.
(36) Zhang, J.; DesMarteau, D. D. *J. Fluorine Chem.* **2001**, *111*, 253−257.
(37) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550−9561.
(38) Dupuis, C.; Adiey, K.; Charruault, L.; Michelet, V.; Savignac, M. *Tetrahedron Lett.* **2001**, *42*, 6523−6526.
(39) Bei, X.; Turner, H. W.; Weinberg, W. H.; Guram, A. S.; Petersen, J. L. *J. Org. Chem.* **1999**, *64*, 6797−6803.