Palladium/P,O-Ligand-Catalyzed Suzuki Cross-Coupling Reactions of Arylboronic Acids and Aryl Chlorides. Isolation and Structural Characterization of (P,O)-Pd(dba) Complex

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The phenyl backbone-derived P,O-ligands **1** and **2** were investigated for their utility as ligands in palladium/ligand-catalyzed Suzuki reactions. The 2-(2′-dicyclohexylphosphinophenyl)-2-methyl-1,3-dioxolane (ligand **1**) in combination with $Pd(dba)_2$ affords an efficient catalyst for general Suzuki reactions of a wide variety of arylboronic acids and aryl chlorides, bromides, and iodides to afford the desired biaryl products in high isolated yields. Arylboronic acids and aryl chlorides containing electron-poor, electron-rich, and ortho substituents participate effectively. In contrast, the structurally related ligand 2-(2′-dicyclohexylphosphinophenyl)-1,3-dioxolane (ligand **2**) was found to be less efficient under similar conditions. The reaction of ligand **1** with $Pd(dba)_2$ affords the complex LPd(dba) (**14**, L = **1**). The NMR spectroscopic and X-ray crystallographic data of complex **14** establish that ligand **1** functions as a P,O-chelating ligand in complex **14**. The reaction of ligand **2** (2 equiv) with $Pd(dba)_2$ and excess 4-^{t}Bu-C_6H_4Br or the ligand displacement reaction of $\{Pd[P(o\text{-tolyl})_3](4\text{-}^t\text{Bu-}C_6H_4)(\mu\text{-Br})\}_2$ with ligand **2** affords the bis-phosphine complex $L_2Pd(4\text{-}^t\text{Bu-}C_6H_4)(Br)$ (**13**, L = **2**). The NMR spectroscopic data of complex **13** establish that ligand **2** in complex **13** functions as a nonchelating ligand. Thus, the higher efficiency of ligand **1** over ligand **2** in Pd/L-catalyzed Suzuki arylation of aryl chlorides can be ascribed to the ability of ligand **1** to generate and stabilize monophosphine P,O-chelating Pd/L intermediates, which appear to be most suitable for Suzuki arylation reactions involving certain substrates and conditions.

Introduction

The Suzuki cross-coupling reactions of arylboronic acids and aryl electrophiles provide an effective and attractive synthetic route to biaryls,[1] which are an important class of organic compounds useful as precursors to pharmaceuticals, polymers, materials, liquid crystals, and ligands. Among the aryl electrophiles investigated, aryl iodides, bromides, and triflates have been found to be the most reactive and are therefore commonly employed.[2,3] The general usefulness of aryl mesylates[4] and diazonium salts[5] as suitable aryl electrophiles has been recently demonstrated, but the utility of the industrially significant aryl chlorides as the aryl electrophiles has remained generally limited to electron-deficient aryl chlorides or nickel-catalyzed reactions.[6,7] Recently, efficient palladium/ligand catalysts for general reactions of arylboronic acids and aryl chlorides were

(1) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, 95, 2457−2483. (b) Suzuki, A. *Pure Appl. Chem.* **1991**, *63*, 419−422. (c) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263−303. (d) Martin, A. R.; Yang, Y. *Acta Chem. Sand.* **1993**, *47*, 221−230. (e) Beletskaya, I. P. *Bull Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1990**, *39*, 2013−2028. (f) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551−564.

(2) Leading references for Suzuki reactions involving aryl iodides and bromides: (a) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513−519. (b) Thompson, W. J.; Gaudino, J. *J. Org. Chem.* **1984**, *49*, 5237−5243. (c) Miller, R. B.; Dungar, S. *Organometallics* **1984**, *3*, 1261−1263. (d) Sato, M.; Miyaura, N.; Suzuki, A. *Chem. Lett.* **1989**, 1405−1408. (e) Wallow, T. I.; Novak, B. M. *J. Org. Chem.* **1994**, *59*, 5034−5037. (f) Watanabe, T.; Miyaura, N.; Suzuki, A. *Synlett* **1992**, 207−210. (g) Marck, G.; Villiger, A.; Buchecker, R. *Tetrahedron Lett.* **1994**, *35*, 3277−3280. (h) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513−519. (i) Fu, J.-m.; Sharp, M. J.; Snieckus, V. *Tetrahedron Lett.* **1988**, *29*, 5459−5462. (j) Bumagin, N. A.; Bykov, V. V.; Beletskaya, I. P. *Bull. Acad. Sci., USSR, Div. Chem. Sci. (Engl. Transl.)* **1989**, *38*, 2206. (k) Hegedus, L. S. *J. Organomet. Chem.* **1993**, *457*, 167−272. (l) Casalnuvo, A. L.; Calabrese, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4324−4330. (m) Genet, J. P.; Blart, E.; Savignac, M. *Synlett* **1992**, 715−717.

(3) Leading references for Suzuki reactions involving aryl triflates: (a) Oh-e, T.; Miyaura, N.; Suzuki, A. *Synlett* **1990**, 221−223. (b) Huth, A.; Beetz, I.; Schumann, I. *Tetrahedron* **1989**, *45*, 6679−6682. (c) Fu, J.-m.; Snieckus, V. *Tetrahedron Lett.* **1990**, *31*, 1665−1668. (d) Oh-e, T.; Miyaura, N.; Suzuki, A. *J. Org. Chem.* **1993**, *58*, 2201−2208.

(4) (a) Percec, V.; Bae, J.-Y.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 1060−1065. (b) Percec, V.; Bae, J.-Y.; Zhao, M.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 176−185. (c) Percec, V.; Bae, J.-Y.; Zhao, M.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 1066−1069. (d) Percec, V.; Bae, J.-Y.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 6895−6903. (e) Percec, V.; Zhao, M.; Bae, J.-Y.; Hill, D. H. *Macromolecules* **1996**, 29, 3727−3735. (f) Percec, V.; Bae, J.-Y.; Zhao, M.; Hill, D. H. *Macromolecules* **1995**, *28*, 6726−6734.

(5) (a) Sengupta, S.; Bhattacharyya, S. *J. Org. Chem.* **1997**, *62*, 3405−3406. (b) Darses, S.; Jeffery, T.; Genet, J.-P.; Brayer, J.-L.; Demoute, J.-P. *Tetrahedron Lett.* **1996**, *37*, 3857−3860.

(6) Earlier examples of Pd-catalyzed Suzuki biaryl cross-couplings involving aryl chlorides: (a) Beller, M.; Fischer, H.; Herrmann, W. A.; Ofele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848−1849. (b) Bumagin, N. A.; Bykov, V. V. *Tetrahedron* **1997**, 53, 14437−14450. (c) Shen, W. *Tetrahedron Lett.* **1997**, *38*, 5575−5578. (d) Cornils, B. *Org. Process Res. Dev.* **1998**, *2*, 121−127. (e) Mitchell, M. B.; Wallbank, P. J. *Tetrahedron Lett.* **1991**, *32*, 2273−2276. (f) Firooznia, F.; Gude, C.; Chan, K.; Satoh, Y. *Tetrahedron Lett.* **1998**, *39*, 3985−3988. (g) Zhang, H.; Chan, K. S. *Tetrahedron Lett.* **1996**, *37*, 1043−1044. (h) Gronowitz, S.; Hornfeldt, A. B.; Kristjansson, V.; Musil, T. *Chem. Scr.* **1986**, *26*, 305−309. (i) Thompson, W. J.; Jones, J. H.; Lyle, P. A.; Thies, J. E. *J. Org. Chem.* **1998**, *53*, 2052−2055. (j) Uemura, M.; Nishimura, H.; Kamikawa, K.; Nakayama, K.; Hayashi, Y. *Tetrahedron Lett.* **1994**, *35*, 1909−1912. (k) Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93−96. (l) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047−1062. (m) Haber, S.; Kleiner, H.-J. US Patent 5,756,804, 1998.

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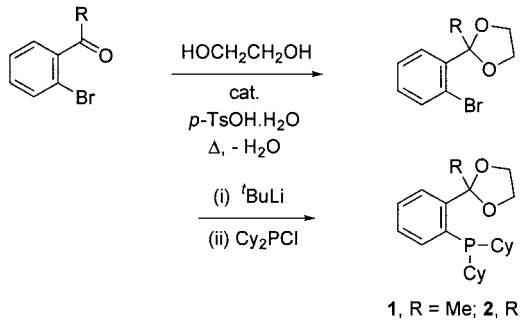
independently reported by the research groups at MIT and Symyx Technologies.[8−10]

As part of our overall program to identify, develop, and utilize high-throughput methods for the discovery of useful materials,[11] a class of phenyl backbone-derived P,O-ligands were identified to be efficient for the general palladium/ligand-catalyzed aminations of aryl bromides, iodides, and chlorides.[12] The key P,O-ligand was subsequently identified to be also suitable for the general palladium/ligand-catalyzed Suzuki reactions of aryl haldies.[10] Details of this Suzuki catalyst discovery study at Symyx Technologies are described herein. The study illustrates that phenyl backbone-derived P,O-ligand **1** provides an efficient palladium/ligand **1** catalyst for general Suzuki cross-coupling reactions of aryl halides including aryl chlorides. The study also illustrates that slight difference in the P,O-ligand structure influences the catalytic efficiency of the palladium/P,O-ligand-catalyzed Suzuki biaryl cross-coupling reactions.

Results

I. Synthesis of Ligands 1 and 2. Ligands **1** and **2** were prepared in two high-yield steps from the commercially available starting materials, 2′-bromoacetophenone and 2-bromobenzaldehyde, respectively, as illustrated in eq 1.[13] The ligands **1** and **2** were purified by recrystallization from deoxygenated methanol solvent and were obtained as white solids and unambiguously characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis.

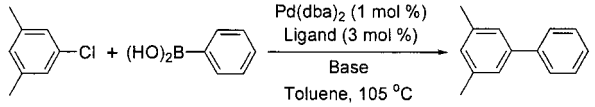


(1)

1, R = Me; **2**, R = H

II. Pd/L (L = 1, 2)-Catalyzed Suzuki Cross-Coupling Reactions of Arylboronic Acids and Aryl Chlorides. The Pd(dba)$_2$/L-catalyzed (dba = dibenzylideneacetone) reaction of 5-chloro-*m*-xylene and phenylboronic acid was chosen as a model reaction for investigating the efficiencies of ligands and bases (Table 1). While ligand **1** was found to be efficient, affording the desired biaryl product in high GC yield, the structurally related ligand **2** was found to be surprisingly less efficient and exhibited lower conversions under otherwise similar reaction conditions.[14] Among the bases investigated, CsF and K_3PO_4 were found to be the most efficient. Toluene and 1,4-dioxane were found to be generally suitable solvents.

Table 1. Base Effects in the Suzuki Reaction of 5-Chloro-*m*-xylene and Phenylboronic Acid[a]



	Conversion %[b]					
	CsF	K_3PO_4	Cs_2CO_3	NaO^{t}Bu	Na_2CO_3[c]	NBu_3
1	75 (100)[d]	75	44	15	10	0
2	14 (23)[d]	21				

[a] Unless indicated otherwise, all reactions were conducted in toluene (4 mL) at 105 °C using 1.0 equiv of 5-chloro-*m*-xylene, 1.5 equiv of phenylboronic acid, 3.0 equiv of base, 1 mol % of Pd(dba)$_2$, and 3 mol % of ligand. [b] Calibrated conversions of starting aryl chloride to the desired biaryl at 3 h, based on GC−MS. [c] Similar result was obtained using toluene/H_2O (3/1) as solvent. [d] Numbers in parentheses correspond to GC−MS conversions at 5 h at reaction temperature of 110 °C.

The utility of the Pd(dba)$_2$/ligand **1** catalyst for general Suzuki biaryl cross-coupling reactions of aryl chlorides was further investigated to determine its scope and limitations.[15] In general and as shown in Table 2, the Pd(dba)$_2$/ligand **1** catalyst was found to exhibit a broad scope. The Pd(dba)$_2$/ligand **1** catalyst was found to be generally efficient in catalyzing the cross-coupling reactions of a wide variety of arylboronic acids and aryl chlorides to afford the desired biaryl products in high isolated yields (Table 2). Arylboronic acids and aryl chlorides containing both electron-poor and electron-rich substituents participated effectively. Aryl chlorides containing ortho substituents also reacted effectively (entries C and J, Table 2). More remarkably, *o*-chlorotoluene reacted efficiently with *o*-tolylboronic acid to afford the desired sterically demanding biaryl product, 2,2′-dimethyl-1,1′-biphenyl, in 91% isolated yield (entry K, Table 2). Aryl bromides and iodides were also found to be suitable substrates (entries G and H, Table 2).

III. Nature of the Pd/L Catalysts. The difference in efficiency of ligands **1** and **2** in Pd/L-catalyzed Suzuki biaryl cross-coupling reaction suggests that the potential catalytic intermediates involved in the catalytic cycle

(7) Ni-catalyzed Suzuki reactions involving aryl chlorides; see ref 6f. See also: (a) Saito, S.; Oh-tani, S.; Miyaura, N. *J. Org. Chem.* **1997**, *62*, 8024−8030. (b) Saito, S.; Sakai, M.; Miyaura, N. *Tetrahedron Lett.* **1996**, *37*, 2993−2996. (c) Indolese, A. F. *Tetrahedron Lett.* **1997**, *38*, 3513−3516.

(8) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3387−3388.

(9) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722−9723.

(10) Bei, X.; Crevier, T.; Guram, A. S.; Jandeleit, B.; Powers, T. S.; Turner, H. W.; Uno, T.; Weinberg, W. H. *Tetrahedron Lett.* **1999**, *40*, 3855−3858.

(11) (a) Danielson, E.; Golden, J. H.; McFarland, E. W.; Reaves, C. M.; Weinberg, W. H.; Wu, X. D. *Nature* **1997**, *389*, 944−948. (b) Boussie, T. R.; Coutard, C.; Turner, H. W.; Murphy, V.; Powers, T. S. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3272−3274. (c) LaPointe, A. M. *J. Combinatorial Chem.* **1999**, *1*, 101−104.

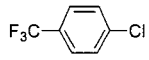
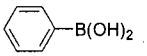
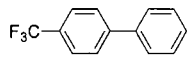
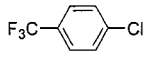
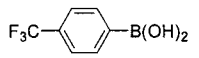
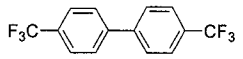
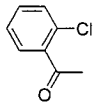
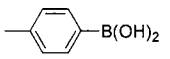
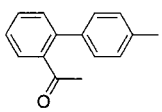
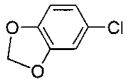
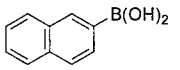
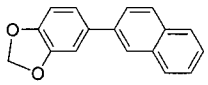
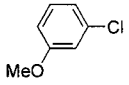
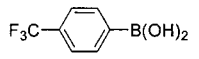
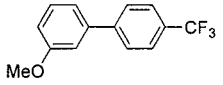
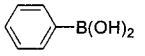
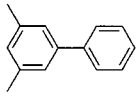
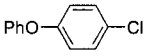
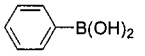
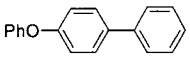
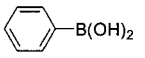
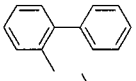
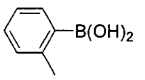
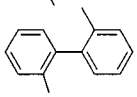
(12) (a) Bei, X.; Uno, T.; Norris, J.; Turner, H. W.; Weinberg, W. H.; Guram, A. S.; Petersen, J. L. *Organometallics* **1999**, *18*, 1840−1853. (b) Bei, X.; Guram, A. S.; Turner, H. W.; Weinberg, W. H. *Tetrahedron Lett.* **1999**, *40*, 1237−1241.

(13) The synthesis and characterization of ligand **1** was described previously; see ref 12a. For general utility of ligand **1** in palladium/ligand-catalyzed amination of aryl chlorides, see ref 12a,b.

(14) The Pd(dba)$_2$/ligand **2** catalyst is suitable for amination of aryl chlorides with both cyclic and acyclic secondary amines (Bei, X.; Guram, A. S. Unpublished results), although the reactions are slower compared to the analogous reactions catalyzed by Pd(dba)$_2$/ligand **1** (ref 12a). For example, Pd(dba)$_2$/ligand **2**-catalyzed reaction of 5-chloro-*m*-xylene with *N*-heptylmethylamine under our standard aryl amination conditions proceeded to completion overnight to afford the desired arylamine product.

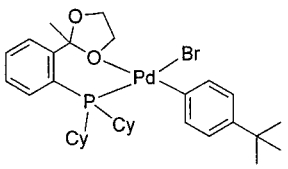
(15) Although all our studies employed Pd(dba)$_2$ as the metal precursor, other suitable Pd(0) or Pd(II) metal complexes could also be used. A variety of different metal complexes have been employed as catalyst precursors or catalysts for Suzuki reactions; see ref 1. Also, while most of our studies utilized a Pd/L ratio of 1/3, Pd/L ratios of 1/1−1.5 are also generally suitable under rigorously air-free conditions.

Table 2. Pd/Ligand 1-Catalyzed Suzuki Cross-Coupling of Arylboronic Acids and Aryl Chlorides[a]

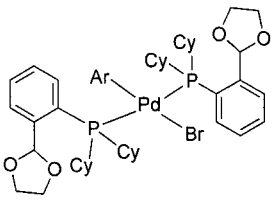
Entry	Aryl Chloride	Arylboronic Acid		Product	Yield%
A[b]			3		92
B			4		97
C			5		83
D			6		96
E			7		93
			8		
F	X = Cl				94
G	X = Br				88
H	X = I				96
I[c]			9		94
J[d]			10		95
K[d]			11		91

[a] General reaction conditions: 1.0 equiv of aryl halide, 1.5 equiv of boronic acid, 3.0 equiv of CsF, 0.5−1 mol % $Pd(dba)_2$, 1.5−3 mol % ligand **1**, 1,4-dioxane or toluene (4 mL), 100−110 °C. Yields correspond to isolated material of >95% purity by GC and NMR. Reaction time = 5−20 h unoptimized, complete conversion of aryl chloride. [b] 80 °C. [c] *o*-Xylene as solvent, 130 °C, 2 mol % $Pd(dba)_2$. [d] 2 mol % $Pd(dba)_2$.

Chart 1



Complex **12**



Complex **13**, Ar = 4-^{t}Bu-C_6H_4

originating from $Pd(dba)_2$/ligand **1** catalyst composition are different from those originating from $Pd(dba)_2$/ligand **2** catalyst composition. We previously established that the chelating monophosphine complex (P,O)Pd(4-^{t}Bu-C_6H_4)Br (**12**) is generated on contacting $Pd(dba)_2$ and excess ligand **1** in the presence of excess 4-^{t}Bu-C_6H_4Br (Chart 1).[12a] The solution- and solid-state structural identity of this complex was unambiguously established by solution NMR spectroscopy and single-crystal X-ray diffraction studies.[12a] Additional related studies were undertaken to gain further insights.

a. Isolation and Characterization of L_2Pd(4-^{t}Bu-C_6H_4)Br (13, L = 2). The reaction of ligand **2** (2 equiv) with $Pd(dba)_2$ and excess 4-^{t}Bu-C_6H_4Br in benzene-d_6 at 80 °C afforded complex **13** (Chart 1). The same complex **13** was also formed and more conveniently isolated from the ligand displacement reaction of the complex [Pd[P(*o*-tolyl)$_3$](4-^{t}Bu-C_6H_4)(μ-Br)]$_2$[16] with ligand **2**. The solution structure of complex **13** was unambiguously established by solution NMR spectroscopic studies. The ^{31}P NMR spectrum in $CDCl_3$ exhibits a single resonance at δ 17.8. This resonance is significantly downfield shifted compared to the corresponding resonance in the ^{31}P NMR spectrum of the free ligand **2** (δ −16.8) and establishes that the P atom is coordinated to the Pd center in complex **13**. The ^{1}H NMR spectrum of complex **13** exhibits two broad partially overlapping resonances at δ 4.19 and 4.18 (eight protons) for two $-OCH_2CH_2O-$ groups. These resonances are nearly identical to those observed for the free ligand **2** (δ 4.14 and 4.02 in $CDCl_3$) and are most consistent with the lack of coordination of any O atom(s) to the Pd center and the presence of two P-coordinating ligands **2** in complex **13**. The presence of only a single resonance in the ^{31}P NMR spectrum of complex **13** further indicates that the two P-coordinated ligands adopt a trans configuration, which makes them equivalent. Attempts to isolate X-ray quality crystals of complex **13** were unsuccessful. The diphenylphosphino analogue of complex **13** has been structur-

(16) (a) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2745−2754. (b) Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030−3039.

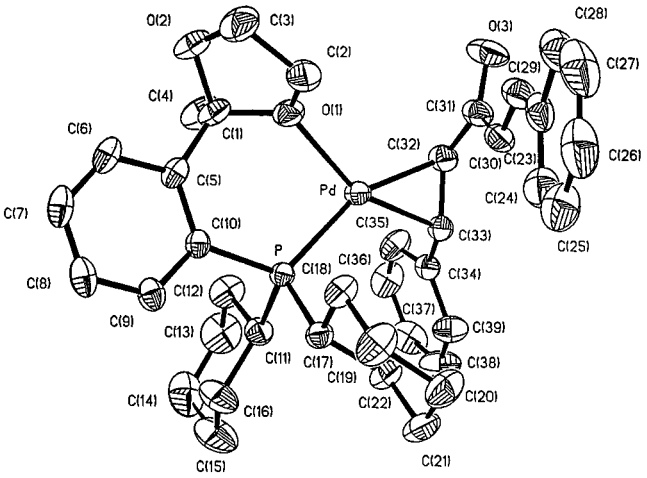
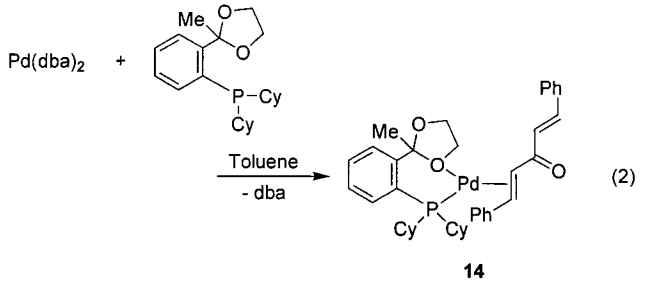


Figure 1. Molecular structure and atom-numbering scheme of complex **14**.

ally characterized previously.[12a]

b. Isolation and X-ray Structure of LPd(dba) (14, L = 1). The complex **14** was formed from the reaction of $Pd(dba)_2$ with excess ligand **1** in toluene at 95 °C and was unambiguously characterized by solution NMR spectroscopic and single-crystal X-ray diffraction studies (eq 2). The ^{31}P NMR spectrum of complex **14** in C_6D_6



14

exhibits a single resonance at δ 27.9. This resonance is downfield shifted compared to the corresponding resonance in the ^{31}P NMR spectrum of ligand **1** (δ −8.3 in C_6D_6)[12a,17] and establishes the coordination of the P atom to the Pd center. The ^1H NMR spectrum of complex **14** exhibits a set of characteristic resonances for the presence of one ligand **1** and one dibenzylideneacetone ligand (see the Experimental Section). The ^1H NMR resonances of the $-OCH_2CH_2O-$ group are broad and slightly shifted compared to those of the free ligand, suggesting the presence of a dynamic interaction between the O atoms and the Pd center.

The X-ray quality crystals of complex **14** were obtained from a cold concentrated toluene solution. The molecular structure of complex **14** is shown in Figure 1, and the crystallographic details and key bond lengths are listed in Tables 3 and 4. The complex **14** adopts a square-planar structure in which ligand **1** is bound to the Pd center through both P and O atoms (Figure 1 and Table 4). The short Pd−O bond distance of 2.249 Å in complex **14** conclusively establishes the coordination of the O atom

(17) Ligand **1**. ^1H NMR (C_6D_6): δ 7.88 (m, 1H, ArH), 7.53 (m, 1H, ArH), 7.24−7.06 (overlapping signals, 2H, ArH), 3.60 (m, 2H, OCHCHO), 3.40 (m, 2H, OCHCHO), 2.19 (s, 3H, CH_3), 2.12−1.0 (22H, CyH). ^{31}P NMR (C_6D_6): δ − 8.3.

Table 3. Crystal Data and Structure Refinements for Complex 14[a]

empirical formula	$C_{46}H_{55}O_3PPd$
MW	793.27
T (K)	295(2)
wavelength (Å)	0.717073
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimensions	a = 11.583(1) Å, α = 81.675(8)°
	b = 12.424(1) Å, β = 86.698(7)°
	c = 14.690(1) Å, γ = 75.112(9)°
volume (Å^3)	2021.1(3)
Z	2
density (calcd) (g/cm^3)	1.304
abs coeff (cm^{-1})	5.37
F(000)	832
crystal size (mm)	0.36 × 0.46 × 0.60
θ range for data collection (deg)	2.06−27.50
index ranges	$-1 \le h \le 15$, $-15 \le k \le 15$, $-19 \le l \le 19$
no. of reflns collected	10 712
no. of ind reflns	9236 (R_{int} = 0.0163)
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	8612/9/468
goodness-of-fit on F^2	1.039
R indices ($I > 2.0\sigma(I)$)	R1 = 0.0397, wR2 = 0.0881
R indices (all data)	R1 = 0.0631, wR2 = 0.0987
largest diff peak and hole (e Å^{-3})	0.463 and −0.339

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma(wi(F_o^2 - F_c^2)^2)/\Sigma(wi(F_o^2)^2)]^{1/2}$, $GOF = [\Sigma(wi(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$.

Table 4. Selected Bond Lengths and Bond Angles of Complex 14

bond lengths (Å)		bond angles (deg)	
Pd−O(1)	2.249(2)	O(1)−Pd−P	87.38(5)
Pd−P	2.2924(7)	C(33)−Pd−P	115.68(6)
Pd−C(32)	2.138(2)	C(32)−Pd−O(1)	117.45(8)
Pd−C(33)	2.065(2)	C(32)−Pd−C(33)	39.52(8)
C(32)−C(33)	1.423(3)	P−Pd−C(32)	155.15(6)
		O(1)−Pd)−C(33)	156.45(7)

to the Pd center.[18] The P−Pd−O bite angle of 87.38(5)° in complex **14** is slightly larger than that observed in the previously characterized (P,O)-Pd(4-^{t}BuC_6H_4)Br (**12**, P,O = ligand **1**, 84.95(9)°) complex. The C(32)−C(33) bond distance and the C(32)−Pd-C(33) bond angle of the dibenzylideneacetone ligand are usual and are similar to those observed previously in the (P,P)-Pd(dba) complex (P,P = bis(diphenylphosphino)ethane).[19,20]

Discussion

The phenyl backbone-derived P,O-ligand **1** affords an efficient Pd/ligand **1** catalyst for the general and efficient Suzuki cross-coupling reactions of arylboronic acid and

(18) The Pd−O bond distance in complex **14** compares favorably with the Pd−O covalent bond distances reported for square planar complexes (2.0−2.16 Å) and is similar to the Pd−O bond distance of the previously characterized complex **12** (2.16 Å); see ref 12a. See also: (a) Kiers, N. H.; Feringa, B. L.; Kooijman, H.; Spek, A. L.; Van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1169−1170. (b) Kaptejin, G. M.; Grove, D. M.; Kooijman, H.; Smeets, W. J.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 526−533. (c) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163−1188 and references therein.

(19) Herrmann, W. A.; Thiel, W. R.; Brossmer, C.; Ofele, K.; Priermeier, T.; Scherer W. *J. Organomet. Chem.* **1993**, *461*, 51−60.

(20) Analogous studies of the reaction of ligand **2** (2 equiv) with Pd(dba)$_2$ under otherwise similar reaction conditions did not afford any unambiguously characterizable complex(es). Both the ^1H and ^{31}P NMR spectra of the reaction mixture exhibited significantly broad resonances.

aryl chlorides. The Pd/ligand **1** catalyst effectively couples a variety of arylboronic acids and aryl chlorides containing electron-poor and electron-rich substituents to afford the desired biaryls in high isolated yields. The catalyst also appears to be suitable for the coupling of sterically demanding ortho-substituted arylboronic acids and aryl chlorides.

The difference in efficiency between the $Pd(dba)_2$/ligand **1** catalyst and the $Pd(dba)_2$/ligand **2** catalyst is surprising given the nearly identical structures of ligands **1** and **2**. This difference in reactivity presumably results from the generation and involvement of structurally different catalytic intermediates. The $Pd(dba)_2$/ligand **1** catalyst system appears to involve "(P,O)-Pd" monophosphine intermediates in which the P,O-ligand coordinates to the Pd center via both the P and O atoms, while the $Pd(dba)_2$/ligand **2** catalyst system appears to involve "$(P,O)_2$-Pd" bisphosphine intermediates in which each of the P,O-ligands coordinates to the Pd center only via the P atom. This is consistent with the isolation and characterization of the structurally different complexes **12** and **13** from the reaction of $Pd(dba)_2$/4-^{t}BuC_6H_4Br with ligands **1** and **2**, respectively, and complex **14** from the reaction of $Pd(dba)_2$ with ligand **1**. In complexes **12** and **14**, one molecule of ligand **1** coordinates to the Pd center via both the P and O atoms, while in complex **13**, two molecules of ligand **2** coordinate to the Pd center only via the P atom and in a trans fashion. Both complexes **14** and **12** represent potential catalytic intermediates of subsequent steps of the catalytic cycle, which suggests that ligand **1** generally favors the generation and stability of monophosphine P,O-chelating (P,O)-Pd intermediates. However, the isolation and characterization of such complexes does not preclude the rapid dissociation and association of the O atom of ligand **1** from the Pd center under catalytic conditions. In fact, such a dynamic behavior, which would classify ligand **1** as a hemilabile ligand,[21a] would be particularly favorable for cross-coupling catalysis. The chelate structures would favor the oxidative addition step, while a sterically crowded nonchelate structure would favor the reductive elimination step of the catalytic cycle.[21b−d] This is also consistent with the fact that the strongly chelating bidentate ligand, bis-1,2-(dicyclohexylphosphino)ethane, is inefficient for analogous Suzuki biaryl cross-coupling reactions of aryl chlorides.[8]

Thus, the efficiency of ligand **1** for $Pd(dba)_2$/ligand **1**-catalyzed Suzuki cross-coupling reactions of arylboronic acid and aryl chlorides can be ascribed to both the overall structure of ligand **1** and the presence of the PCy_2 unit. As described above, the rigid phenyl backbone-derived structure of ligand **1** favors the generation and stability of the chelating monophosphine "(P,O)-Pd" intermediates, which appear to be most suitable for Suzuki and related cross-coupling catalysis involving certain substrates and conditions,[22] while the PCy_2 unit makes the Pd center sufficiently electron-rich to promote oxidative addition of the usually unreactive aryl chlorides.

Overall, the catalytic performance of Pd/ligand **1** catalyst for Suzuki biaryl cross-coupling of aryl chlorides is similar to that of the recently described Pd/^{t}Bu$_3$P[8] and Pd/P,N[9] (P,N = 1-(*N*,*N*-dimethylamino)-1′-(dicyclohexylphosphino)biphenyl) catalysts, all three of which constitute the current state of the art catalysts for the Suzuki arylation of aryl chlorides. However, unlike the Pd/^{t}Bu$_3$P[8] and Pd/P,N[9] catalysts, the Pd/ligand **1** catalyst was observed to be most efficient at slightly higher temperatures under the conditions investigated. It also appears that the Pd/ligand **1** and Pd/P,N catalysts, both of which involve potentially chelating hemilabile ligands, offer higher catalyst turnovers than the Pd/^{t}Bu$_3$P catalysts (typically ca. 100−200 for Pd/ligand **1** and Pd/P,N catalysts vs ca. 33 for Pd/^{t}Bu$_3$P catalyst).[8,9] This suggest that the ketal group in ligand **1** (similar to the amino group in the P,N ligand) additionally contributes to the enhanced stability of the catalyst.

Conclusions

We have demonstrated that the phenyl backbone-derived P,O-ligand **1** provides an effective, convenient, and general Pd/ligand **1** catalyst for efficient Suzuki cross-coupling reactions of arylboronic acids and aryl chlorides. The effectiveness of Pd/ligand **1** catalyst results from the presence of both the PCy_2 and ketal units that favor the generation and stability of electron-rich chelating monophosphine (P,O)-Pd intermediates. Such (P,O)-Pd intermediates appear to be ideally suitable for Suzuki aryl chloride arylations involving this class of ligands. The Pd/ligand **1** catalyst along with the previously reported Pd/^{t}Bu$_3$P and Pd/P,N catalysts represent the current state of the art catalysts for the general Pd/L-catalyzed Suzuki arylation of aryl chlorides.

Experimental Section

General Comments. All reactions were performed under argon atmosphere in oven-dried glass Schlenk tubes using standard Schlenk techniques. All aryl halides, arylboronic acids, bases (CsF, NaO^{t}Bu, K_3PO_4, NBu_3, Cs_2CO_3, and Na_2CO_3), bis(dibenzylideneacetone)palladium, diethyl ether, methylene chloride, benzene, toluene, *o*-xylene, and 1,4-dioxane were purchased from commercial sources and used as such. All solvents were of the anhydrous, sure-seal grade. Ligand **1** and $\{Pd[P(o\text{-tolyl})_3](4\text{-}^t\text{Bu-}C_6H_4)(\mu\text{-Br})\}_2$ were prepared according to literature procedures.[12a,16] The detailed procedure described for the synthesis and isolation of compound **3** was generally followed for all Pd/Ligand **1**-catalyzed Suzuki reactions of arylboronic acids with aryl halides. All Pd/Ligand **1**-catalyzed Suzuki reactions were performed until complete consumption of the starting aryl halide, but the reaction times and conditions have not been thoroughly optimized. Column chromatography was performed using commercially available silica gel 60 (particle size: 0.063−0.100 mm), hexanes, and ethyl acetate. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained

(21) For a recent review on hemilabile ligands and their transition-metal coordination chemistry, see: (a) Slone, S. C.; Weinberger, D. A.; Mirkin, C. A. *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons: New York, 1999; Vol. 48, pp 233−350. The Pd/L-catalyzed Suzuki biaryl cross-coupling reactions proceed via the oxidative addition of an aryl halide to an "L_nPd^0" intermediate, formation of "$L_nPd^{II}(Ar)(Ar')$" intermediate, followed by reductive elimination of biaryl and regeneration of "L_nPd^0"; see ref 1. For mechanistic studies and discussion of the influence of ligand-chelating structures on the rate of oxidative addition and reductive elimination, see: (b) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994; p 27 and references therein. (c) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1655−1664. (d) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665−1673.

(22) However, the efficient utility of the recently described monodentate phosphine, ^{t}Bu$_3$P, in Pd/L-catalyzed general Suzuki biaryl cross-coupling reactions of aryl chlorides suggest that chelation may not be required if other ligand structural properties are favorable. The steric properties of the ^{t}Bu$_3$P ligand presumably are sufficient for the generation and involvement of the most desired mono-phosphine "LPd" intermediates. Alternatively, the desired monophosphine "LPd" intermediates could also be accessible because of steric and electronic properties of certain aryl halide substrates and reaction conditions.

using a 300 MHz FT-NMR spectrometer. Chemical shifts in ^1H and ^{13}C NMR spectra were calibrated with reference to the chemical shift of residual protiated solvent. Chemical shifts in ^{31}P NMR spectra were calibrated with reference to 85% H_3PO_4; a negative value of chemical shift denotes resonance upfield from H_3PO_4. *J* values are reported in Hz. Elemental analyses were performed by E & R Microanalytical Laboratory Inc., Parsippany, NJ.

2-(2′-Dicyclohexylphosphinophenyl)-1,3-dioxolane (Ligand 2). A solution of 2-(2′-bromophenyl)-1,3-dioxolane (2.0 g, 8.7 mmol) in anhydrous diethyl ether (50 mL) was cooled to − 78 °C. A solution of *tert*-butyllithium (10.3 mL, 1.7 M solution in hexane, 17.5 mmol) was added dropwise with stirring. The reaction was allowed to stir for 1 h at −78 °C. Chlorodicyclohexylphosphine (2.43 g, 10.5 mmol) was added dropwise via a syringe at −78 °C with stirring. The reaction was allowed to warm to room temperature and stirred for an additional 12 h. Deoxygenated H_2O (40 mL) was added slowly. The organic layer was separated. The aqueous layer was washed with diethyl ether (25 mL), and the combined organic phase was concentrated under vacuum to afford a yellow oil. The oil was triturated with air-free methanol (5 mL) at room temperature to afford ligand **2** (2.4 g, 80% yield) as a crystalline white solid. ^{31}P NMR ($CDCl_3$): δ −16.8. ^1H NMR ($CDCl_3$): δ 7.65 (br m, 1H, ArH), 7.47 (d, J = 7.2, 1H, ArH), 7.34 (m, 2H, ArH), 6.63 (d, J = 6.9, 1H, CH), 4.14 (m, 2H, OCHCHO), 4.02 (m, 2H, OCHCHO), 2.0−0.8 (overlapping signals, 22H, CyH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.0, 143.7, 132.4, 128.9, 128.3, 126.4, 101.3 (J_{PC} = 31, OCO), 65.5 (OCH_2), 34.0 (J_{PC} = 12), 30.5 (J_{PC} = 17), 29.2 (J_{PC} = 8), 27.1 (2C), 26.3. Anal. Calcd for $C_{21}H_{31}O_2P$: C, 72.80; H, 9.02, P, 8.94. Found: C, 72.79; H, 9.01; P, 8.77.

General Procedure for the Study of Base Effects in the Suzuki Reaction of 5-Chloro-*m*-xylene and Phenylboronic Acid (Table 1). A solid mixture of phenylboronic acid (1.5 mmol), base (3.0 mmol), $Pd(dba)_2$ (10 μmol), and ligand (30 μmol) was thoroughly evacuated and purged with argon. 5-Chloro-*m*-xylene (1.0 mmol) and toluene (4 mL) were added, and the reaction was heated at 100−105 °C. The reaction was monitored by GC−MS for conversion of the starting aryl chloride to desired biaryl product. Only trace amounts, if any, of the homocoupled byproduct, biphenyl, were detected in all cases. Calibrated conversions are reported in Table 1.

4-Trifluoromethylbiphenyl (3). A solid mixture of phenylboronic acid (177 mg, 1.5 mmol), CsF (442 mg, 2.9 mmol), $Pd(dba)_2$ (3 mg, 5 μmol), and ligand **1** (6 mg, 17 μmol) was weighed in air and loaded into a Schlenk reaction tube. The reaction tube was thoroughly evacuated and purged with argon. 4-Chlorobenzotrifluoride (0.13 mL, 0.97 mmol) and 1,4-dioxane (4 mL) were added, and the reaction was heated at 80 °C for 16 h. The reaction was taken up in ether (100 mL) and washed with H_2O (30 mL) and brine (30 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using hexanes/ethyl acetate (4/1) as eluant to afford compound **3** as a white solid (198 mg, 92%) after drying under vacuum.^1H NMR ($CDCl_3$): δ 7.69 (s, 4H), 7.59 (d, J = 7.8, 2H), 7.47 (t, J = 6.9, 2H), 7.41 (d, J = 6.9, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.7, 139.8, 129.0, 128.2, 127.4, 127.3, 125.7 (q, J = 4). Anal. Calcd for $C_{13}H_9F_3$: C, 70.27; H, 4.08. Found: C, 70.31; H, 3.91.

4,4′-Bis(trifluoromethyl)-1,1′-biphenyl (4).[23] Compound **4** was obtained as a white solid (273 mg, 97%) from the reaction of 4-(trifluoromethyl)phenylboronic acid (277 mg, 1.5 mmol), CsF (442 mg, 2.9 mmol), $Pd(dba)_2$ (6 mg, 10 μmol), ligand **1** (11 mg, 31 μmol), and 1,4-chlorobenzotrifluoride (0.13 mL, 0.97 mmol) in 1,4-dioxane at 95 °C for 12 h. ^1H NMR ($CDCl_3$): δ 7.80 (d, J = 8.7, 4H), 7.76 (d, J = 8.7, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 127.6, 125.9 (q, J = 4), ipso carbons were not observed.

2-Acetyl-4′-methyl-1,1′-biphenyl (5).[24] Compound **5** was obtained as a yellowish oil (176 mg, 83%) from the reaction of 4-methylphenylboronic acid (204 mg, 1.5 mmol), CsF (456 mg, 3.0 mmol), $Pd(dba)_2$ (6 mg, 10 μmol), ligand **1** (11 mg, 31 μmol), and 2′-chloroacetophenone (0.13 mL, 1.0 mmol) in 1,4-dioxane (4 mL) at 100 °C for 17.5 h. ^1H NMR ($CDCl_3$): δ 7.52 (d, J = 8.4, 1H, ArH), 7.47 (d, J = 7.2, 1H, ArH), 7.38 (t, J = 7.2, 2H, ArH), 7.22 (s, 4H, ArH), 2.39 (s, 3H, $C(O)CH_3$), 2.00 (s, 3H, $ArCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 205.1, 140.9, 140.5, 137.8, 137.7, 130.6, 130.2, 129.4, 128.7, 127.8, 127.2, 30.4, 21.2.

5-(2′-Naphthalene)-1,3-benzodioxole (6). Compound **6** was obtained as an off-white solid (275 mg, 96%) from the reaction of 2-naphthaleneboronic acid (297 mg, 1.73 mmol), CsF (524 mg, 3.45 mmol), $Pd(dba)_2$ (6.6 mg, 11 μmol), ligand **1** (12 mg, 33 μmol), and 5-chloro-1,3-benzodioxole (0.12 mL, 1.15 mmol) in 1,4-dioxane (4 mL) at 100 °C for 7 h. ^1H NMR ($CDCl_3$): δ 7.95 (s, 1H, ArH), 7.90−7.80 (m, 3H, ArH), 7.66 (d/d, J = 8.4/1.8, 1H, ArH), 7.52−7.40 (m, 2H, ArH), 7.21−7.15 (m, 2H, ArH), 6.92 (d, J = 8, 1H, ArH), 6.01 (s, 2H, OCH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 148.2, 147.1, 138.2, 135.5, 133.6, 132.4, 128.3, 128.0, 127.6, 126.3, 125.7, 125.4, 125.3, 120.9, 108.6, 107.9, 101.2. Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.33; H, 4.88.

3-Methoxyl-4′-trifluoromethyl-1,1′-biphenyl (7). Compound **7** was obtained as a colorless oil (223 mg, 90%) from the reaction of 4-trifluoromethylphenylboronic acid (279 mg, 1.47 mmol), CsF (447 mg, 2.94 mmol), $Pd(dba)_2$ (5.6 mg, 10 μmol), ligand **1** (11 mg, 31 μmol), and 3-chloroanisole (0.12 mL, 0.98 mmol) in 1,4-dioxane at 100 °C for 12 h. ^1H NMR ($CDCl_3$): δ 7.68 (4H, ArH), 7.38 (t, J = 8.1, 1H, ArH), 7.17 (d, J = 7.2, 1H, ArH), 7.12 (t, J = 2.1, 1H, ArH), 6.95 (d/d, J = 8.4/2.1, 1H, ArH), 3.87 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.1, 144.6, 141.2, 130.0, 127.5, 125.6 (q, J = 4), 119.7, 113.4, 113.1, 55.3. Anal. Calcd. for $C_{14}H_{11}F_3O$: C, 66.66; H, 4.40. Found: C, 66.75; H, 4.35.

3,5-Dimethylbiphenyl (8).[9] Compound **8** was obtained as a colorless oil (178 mg, 94%; 166 mg, 88%; 170 mg, 96%) from the reaction of phenylboronic acid (190 mg, 1.56 mmol), CsF (473 mg, 3.12 mmol), $Pd(dba)_2$ (6 mg, 10 μmol), ligand **1** (11 mg, 31 μmol), and 5-halo-*m*-xylene (0.14 mL, 1.0 mmol; halo = chloride, bromide, iodide, respectively) in toluene at 100−110 °C for 5−20 h. ^1H NMR ($CDCl_3$): δ 7.64 (d, J = 8.1, 2H, ArH), 7.47 (t, J = 7.7, 2H, ArH), 7.35 (t, J = 7.5, 1H, ArH), 7.27 (s, 2H, ArH), 7.05 (s, 1H, ArH), 2.44 (s, 6H, $ArCH_3$'s). ^{13}C NMR ($CDCl_3$): δ 141.5, 141.3, 138.2, 128.9, 128.6, 127.2, 127.0, 125.1, 21.4.

4-Phenylbiphenyl Ether (9).[25] Compound **9** was obtained as an off-white solid (230 mg, 94%) from the reaction of phenylboronic acid (181 mg, 1.5 mmol), CsF (451 mg, 3.0 mmol), $Pd(dba)_2$ (11 mg, 19 μmol), ligand **1** (22 mg, 61 μmol), and 4-chlorobiphenyl ether (0.17 mL, 0.99 mmol) in *o*-xylene (4 mL) at 130 °C for 20 h. ^1H NMR ($CDCl_3$): δ 7.60−7.50 (m, 4H), 7.47−7.27 (m, 5H), 7.16−7.00 (m, 5H).

2-Methylbiphenyl (10).[8] Compound **10** was obtained as a colorless oil (164 mg, 94.8%) from the reaction of phenylboronic acid (188 mg, 1.54 mmol), CsF (469 mg, 3.09 mmol), $Pd(dba)_2$ (11.8 mg, 21 μmol), ligand **1** (22 mg, 61 μmol), and 2-chlorotoluene (0.12 mL, 1.03 mmol) in toluene (4 mL) at 100 °C for 13.5 h. ^1H NMR ($CDCl_3$): δ 7.44−7.38 (m, 2H, ArH), 7.38−7.30 (m, 3H, ArH), 7.30−7.20 (m, 4H, ArH), 2.28 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.9, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 20.4.

2,2′-Dimethyl-1,1′-biphenyl (11).[8] Compound **11** was obtained as a yellowish oil (171 mg, 91%) from the reaction of 2-methylphenylboronic acid (210 mg, 1.54 mmol), CsF (469 mg, 3.09 mmol), $Pd(dba)_2$ (11.8 mg, 21 μmol), ligand **1** (22 mg, 61 μmol), and 2-chlorotoluene (0.12 mL, 1.03 mmol) in toluene (4 mL) at 105 °C for 13 h. ^1H NMR ($CDCl_3$): δ 7.32−7.18 (m, 6H, ArH), 7.13 (d, J = 6.2, 2H, ArH), 2.08 (s, 6H, CH_3's). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.6, 135.8, 129.8, 129.3, 127.1, 125.5, 19.8.

(23) Marcial, M.-M.; Montserrat, P.; Roser, P. *J. Org. Chem.* **1996**, *61*, 2346−2351.

(24) Nello, R. *Lab. Chim. Org. Struct., Fac. Sci. Paris, Paris, Fr. Ann. Chim.* **1970**, *5*, 119−127.

(25) Commercially available.

$L_2Pd(4\text{-}^tBu\text{-}C_6H_4)Br$ (L = 2, Complex 13). Methylene chloride (4 mL) was added to a mixture of $[Pd[P(o\text{-tolyl})_3](4\text{-}^tBu\text{-}C_6H_4)(\mu\text{-}Br)]_2$ (256 mg, 0.20 mmol) and ligand **2** (284 mg, 0.8 mmol) at room temperature under argon. The mixture was stirred for 4 h at room temperature, and the solvent was removed under vacuum. The crude product was further purified by recrystallization from methylene chloride and heptane (1/20) at −30 °C, yielding complex **13** as yellow crystalline solid. ^{31}P NMR ($CDCl_3$): δ 17.8. ^1H NMR ($CDCl_3$): δ 7.76 (d/d, J = 7.8/1.2, 2H, ArH), 7.35 (t, J = 7.7, 2H, ArH), 7.28 (br, 2H, ArH), 7.05 (t, J = 7.5, 2H, ArH), 6.60 (br, 2H, ArH), 6.40 (d, J = 7.5, 2H, CH), 6.26 (br, 2H, ArH), 4.19 (br, 4H, OCHCHO), 4.18 (br, 4H, OCHCHO), 1.11 (9H, $C(CH_3)_3$, overlap with CyH signals), 2.5−1.0 (overlapping signals, 44H, CyH). ^{13}C NMR ($CDCl_3$): δ 144.8 (J_{PC} = 4), 144.6, 139.6, 136.0, 131.4 (J_{PC} = 31), 130.3, 129.0, 128.1, 127.6, 123.1, 100.9 (J_{PC} = 7), 65.4, 31.4, 31.2, 30.5, 28.1, 27.8, 26.5. Anal. Calcd for $C_{52}H_{75}BrO_4P_2Pd$: C, 61.69; H, 7.47; P, 6.12. Found: C, 61.39; H, 7.50; P, 5.96.

LPd(dba) (L = 1, Complex 14). Toluene-d_8 (0.5 mL) was added to an NMR tube containing $Pd(dba)_2$ (20 mg, 35 μmol) and ligand **1** (12.5 mg, 35 μmol) under argon. The mixture was heated at 95 °C for 1 h, yielding complex **14** as the only NMR-detectable phosphorus-containing product. Cryatals suitable for X-ray diffraction analysis were grown from the toluene solution. ^{31}P NMR (C_6D_6): δ 27.9. ^1H NMR (C_6D_6): δ 7.51 (d, J = 7.2, 2H), 7.4−6.7 (overlapping signals, 16H), 3.65 (br, 2H, OCHCHO), 3.27 (br, 2H, OCHCHO), 1.99 (s, 3H, CH_3, overlap with CyH signals), 2.5−0.7 (overlapping signals, 22H, CyH).

X-ray Crystallography. A crystal of compound **$14\cdot C_7H_8$** was sealed in a glass capillary and then optically aligned on the goniostat of a Siemens P4 X-ray diffractometer. The reflections that were used for the unit cell determination were located and indexed by the automatic peak search routine provided with XSCANS.[26] The intensities of three standard reflections, which were measured after every 100 reflections, showed no indication of crystal decomposition or sample movement. The raw data were collected for Lorentz-polarization effects. Initial coordinates for the non-hydrogen atoms were determined by a combination of heavy atom methods and difference Fourier calculations performed with the algorithms provided in SHELXTL-IRIS operating on a Silicon Graphic Iris Indigo workstation. The hydrogen atom positions were idealized with isotropic temperature factors at 1.2 times that of the adjacent carbon. The positions of methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. The atomic coordinates for the hydrogen atoms attached to C(32) and C(33) were refined. The crystallographic asymmetric unit also contained a molecule of toluene, which was located in a general position within the unit cell. The six C−C bond distances within the phenyl ring and the C−C(Me) distances were restrained at 1.40 ± 0.02 Å and 1.54 ± 0.02 Å, respectively. Crystal data and refinement parameters are summarized in Table 3. Further details of the crystallographic information are provided in the Supporting Information.

Note Added in Proof. The Pd/Imidazol-2-ylidene-catalyzed efficient Suzuki cross-coupling reactions of aryl chlorides with arylboronic acids were described recently.[27]

Supporting Information Available: Tables of final positional parameters, isotropic and anisotropic displacement for all atoms, and bond lengths and angles for complex **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) XSCANS (version 2.0) is a diffractometer control system developed by Siemens Analytical X-ray Instruments, Madison, WI.

(27) Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804−3805.