m-Terphenyl Anchored Palladium Diphosphinite PCP-Pincer Complexes That Promote the Suzuki−Miyaura Reaction Under Mild Conditions

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Diphosphinite PCP-pincer pro-ligands anchored by a *meta*-terphenyl backbone were synthesized. These pro-ligands, [2,6-(2-$Ph_2POC_6H_4)_2C_6H_3X$] (**3a** X = I, **3b** X = Br) and [2,6-(2-$^i Pr_2POC_6H_4)_2C_6H_3X$] (**4a** X = I, **4b** X = Br) upon reaction with $Pd_2(dba)_3$ yield PCP palladium pincer complexes [2,6-(2-$Ph_2POC_6H_4)_2C_6H_3PdX$] (**5a** X = I, **5b** X = Br) and [2,6-(2-$^i Pr_2POC_6H_4)_2C_6H_3PdX$] (**6a** X = I, **6b** X = Br). The structures of **5a**−**b** and **6a**−**b** were determined by single crystal X-ray diffraction analyses. Complexes **5b** and **6b** were evaluated for their efficacy in promoting catalytic Suzuki−Miyaura CC coupling reactions. A variety of aryl bromides efficiently underwent CC coupling reactions with *p*-tolylboronic acid with high yields in the presence of either **5b** or **6b**. Compound **6b** also proved to be a very active pro-catalyst for the coupling of aryl chlorides with *p*-tolylboronic acid. Excellent to good yields (in some cases greater than 90%) were achieved even with electron rich or sterically hindered aryl chlorides.

Introduction

Since its introduction in 1979,[1] the Suzuki−Miyaura reaction has become very important to modern synthetic chemists.[2−7] This catalytic CC coupling reaction between aryl halides and aryl boronic acids to form biaryls can occur under mild conditions and tolerates a wide variety of functional groups. In addition, boronic acids are of low toxicity and their reaction byproducts are easily separated from the desired product. As a result of its utility, much attention has been paid to improving methods and finding new applications for the Suzuki−Miyaura reaction.[8,9] The development of better catalysts has received particularly significant attention.[10,11] Complexes have ultimately been reported which show impressive catalytic activity in the Suzuki−Miyaura reaction at room temperature,[12,13] when using hindered substrates,[14] when using aryl chlorides,[15] or with very low catalyst loadings.[16,17]

Pincer ligand complexes have been recognized for their thermal and chemical stability since they were first reported in the 1970s.[18] More recently, enormous attention has been paid to these terdentate complexes for the development of new palladium catalysts.[19,20] Numerous palladium pincer complex variations have been tested for catalytic activity in a variety of CC coupling reactions. For example, palladium pincer complexes of 1,3-bis(2-pyridyloxy)benzene have been reported to have extremely high turnover numbers (TON = 8.4×10^8) in Heck coupling reactions.[21] Other researchers have used chiral substituents to create a chiral pocket around palladium for asymmetric catalysis.[22−48] For example, enantiomeric excesses

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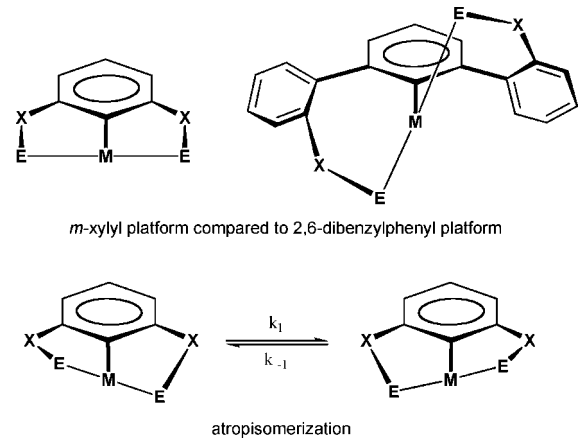
as high as 83% have been reported for asymmetric Michael reactions catalyzed by bispyrroloimidazolone NCN palladium pincer complexes.[34] In regard to the Suzuki−Miyaura reaction, palladium pincer complexes have recently been reported which act as effective catalysts for the coupling of aryl chlorides with aryl boronic acids.[49] Inspired by such developments, we set out to examine the catalytic properties of pincer complexes recently developed in our laboratories.

These particular pincer complexes are constructed upon a triaryl ring backbone (*m*-terphenyl). A *m*-terphenyl backbone was designed as it should yield more rigid pincer and nonplanar (globally) complexes, as compared to those anchored by *m*-xylyl and related frameworks (Chart 1, left).[50] Control of ligand dynamics is key to achieving well defined steric profiles and for projecting possible chirality. For nonplanar pincer ligands, a C_2-symmetric environment can be produced, but for many pincer complexes interconversion between two possible atropisomers can be facile (Chart 1, right). We have shown that *m*-terphenyl based pincer complexes maintain a nonplanar conformation.[51] Herein we examine pincer complexes containing phosphinite groups and have evaluated their catalytic activity for the Suzuki−Miyaura reaction using a variety of aryl bromides and chlorides. The catalytic activity of these complexes at different reaction temperatures was also examined.

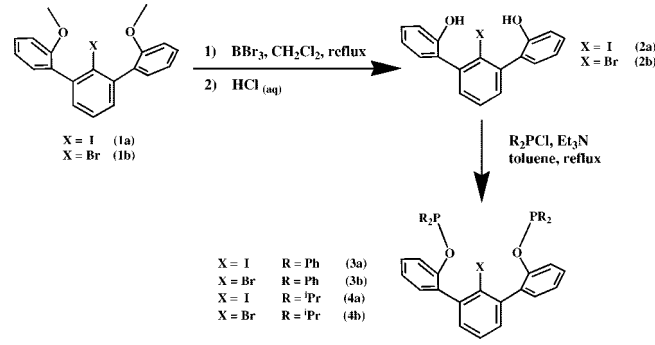
Chart 1



Results and Discussion

Synthesis of Diphosphinite Pro-Ligands. Compounds **1a** and **1b** were synthesized following standard procedures for synthesis of *m*-terphenyls.[52,53] Compound **1b** was obtained in 61% yield by use of bromine in place of iodine used in procedure for **1a**. The ^{1}H NMR spectra of **1a** and **1b** are consistent with characterization of **1a** reported in the literature.[54−56] Two isomers of **1a** and **1b** are indicated by two individual peaks near 3.8 ppm whose combined integrals indicate six protons relative to the signals for the eleven protons in the aromatic region. It is reasonable to ascribe these species as *syn*- and *anti*-isomers, resulting from different conformations of the flanking phenyl rings about the aryl-aryl bonds.

Scheme 1



The dimethoxy-*m*-terphenyls, **1a-b** were converted to dihydroxy compounds **2a** and **2b** by demethylation promoted by BBr_3 (Scheme 1).[57] While it was reported that demethylation of the nonhalogenated analog, 2,2"-dimethoxy-*m*-terphenyl (**1c**, X = H, Scheme 1) required only one equivalent of BBr_3, full conversion of **1a−b** necessitated use of two equivalents of BBr_3. Workup with HCl followed by purification via precipitation from CH_2Cl_2 with hexanes gave **2a** and **2b** in 88 and 90% yields, respectively.

Diphosphinite pro-ligands **3a−b** and **4a−b** were synthesized from **2a−b** following procedures analogous to those reported for the syntheses of R_2POPh and 1,3-$(R_2PO)_2Ph$. Compounds **2a** and **2b** thus provided **3a** and **3b**, respectively, after a 3 h reflux in toluene with chlorodiphenylphosphine in the presence

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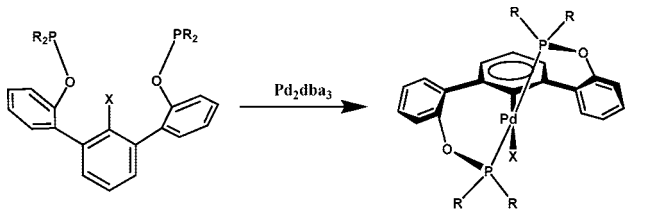
Scheme 2. Synthesis of Palladium Pincer Complexes



				$^{31}P\{^1H\}$ δ
X = I	R = Ph	(5a)	79%	118.2
X = Br	R = Ph	(5b)	70%	118.2
X = I	R = ^{i}Pr	(6a)	64%	153.3
X = Br	R = ^{i}Pr	(6b)	57%	152.6

of excess triethylamine. Compounds **4a**- **b** were synthesized in an analogous manner using chlorodiisopropylphosphine. Monitoring of the reaction progress by ^{31}P and ^1H NMR spectroscopic analyses of reaction aliquots showed formation of both **4a** and **4b** required longer (20 h) reaction times compared to **3a**−**3b**.

Pro-ligands **3a**−**b** were isolated as sticky tan solids and **4a**−**b** were isolated as pale yellow oils. The $^{31}P\{^1H\}$ NMR resonances of the diphosphinite ligands are in agreement with the reported values for similar phosphinite and diphosphinite ligands.[58,59] Spectra of **3a** and **3b** both showed $^{31}P\{^1H\}$ NMR resonances at δ 111.8, while **4a** and **4b** displayed peaks at δ 146.7 and 146.9, respectively. The susceptibility of these compounds to oxidation made complete purification difficult. Reports for related diphosphinite ligands indicated that further purification may not be required for the formation and isolation of complexes with palladium.[59] Diphosphinite pro-ligands **3a**−**b** and **4a**−**b** were thus used without further purification.

Synthesis of Diphosphinite Pincer Complexes. The pincer complexes **5a**−**b** and **6a**−**b** were readily synthesized from ligand precursors by reaction with 0.5 equivalents of Pd_2dba_3 (dba = dibenzylideneacetone) in benzene at room temperature (Scheme 2).[44] Reaction progress was monitored using $^{31}P\{^1H\}$ NMR spectroscopy to observe the consumption of **3a**−**b** or **4a**−**b**. For the synthesis of **5a**−**b**, complete consumption of **3a**−**b** was observed after reacting for 1 h. The synthesis of **6a** and **6b**, however, required a 20 h reaction time for full reaction. The air stable palladium pincer complexes were readily purified by column chromatography. Complexes **5a**−**b** were easily purified by first eluting dibenzylideneacetone with 10% ethyl acetate in hexanes followed by elution of the desired complex with $CHCl_3$. Complexes **6a**−**b** required slightly more care to purify as these metal complexes eluted before dibenzylideneacetone with 10% ethyl acetate in hexanes.

All four metal complexes were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis. As with similar diphosphinite complexes, a small downfield shift was observed for the phosphorus resonance of the metal complex relative to the free ligand.[35] This shift was 8−9 ppm for the bis(diphenylphosphinite) complexes **5a**−**b**. The bis(diisopropylphosphinite) complexes **6a**−**b** had a downfield shift of approximately 6 ppm relative to the starting ligands **4a**−**b**. The complexes were found to have high stability to air as they remained unchanged in solution after several days of exposure to air.

X-Ray Crystallographic Analyses. Single crystal X-ray diffraction analysis was used to determine the structures of the palladium complexes. The structures of **5a**−**b** are shown in Figure 1 and **6a**−**b** in Figure 2. As expected, these diphosphinite complexes are structurally similar to [2,6-(2-Ph_2PCH_2-$C_6H_4)_2C_6H_3PdBr$] (**7**), a diphosphine *m*-terphenyl pincer complex that was reported previously.[50] Key bond lengths and angles about the palladium centers in **5a**−**b**, **6a**−**b**, and **7** are summarized in Table 1. The iodide analogs **5a** and **6a** differ slightly from their respective bromide counterparts **5b** and **6b** with regard to the Pd-X bond which is longer when X = I than when X = Br. Complexes **5a**−**b** are very similar to **7**.

Complexes **5a**−**b** and **7** exhibit pseudo square planar geometries around their Pd(II) centers and crystallographically imposed C_2 axes of symmetry passing through the C(1)−Pd−X bond. A twist angle, Φ, may be defined for the angle between the plane of the phenyl ring containing C1 and the plane containing palladium and the four atoms directly attached to it. Complex **7**, with Φ = 76.7°, has the highest twist angle of any reported pincer complex. Complex **5a** (Φ = 73.9°) and **5b** (Φ = 73.8°) are only slightly less twisted than **7**.

The structures of complex **6a**−**b** have a few notable differences compared to complexes **5a**−**b** and **7**. These differences arise from the steric effects of the relatively bulky isopropyl groups in **6a**−**b** that cause the geometry around the palladium atom in **6a**−**b** to deviate somewhat from planarity. Steric interactions between the isopropyl groups and the halogen atom force the halogen atom out of the plane containing C(1), P(1), P(2), and Pd. As a result, in **6a**−**b**, the C(1)−Pd−X bond angles are somewhat smaller than the 180 °C(1)−Pd−X bond angles found in **5a**−**b**. Another slight difference between **6a**−**b** and **5a**−**b** is a 10% decrease in twist angle for complexes **6a**−**b** relative to **5a**−**b**. Even with these differences, the structures of **6a**−**b** are still quite similar to **5a**−**b** and **7**.

Suzuki−Miyaura CC Cross Coupling Reactions Using Complexes 5b and 6b. Preliminary screening of **5a**−**b** and **6a**−**b** as catalysts for the coupling of phenylboronic acid with several aryl bromides revealed that the iodide compounds, **5a** and **6a**, had nearly the same catalytic activity as their respective bromide counterparts, **5b** and **6b**. Examination of **5b** and **6b** for catalytic activity in Suzuki−Miyaura cross coupling reactions of *p*-tolylboronic acids with a variety of aryl bromides and chlorides was thus undertaken (Scheme 3). Experiments were conducted in refluxing 1,4-dioxane in the presence of excess Cs_2CO_3, and the products were isolated by filtering reaction mixtures through a thin pad of silica gel followed by evaporation of solvent under reduced pressure. This method proved successful in most cases to give the product in >95% purity as estimated by ^1H NMR spectroscopy.

Complex **5b** proved to be an excellent catalyst precursor for the coupling reaction between *p*-tolylboronic acid and a variety of aryl bromides (Table 2). These tests were carried out in refluxing 1,4-dioxane in the presence of Cs_2CO_3 with 1 mol% of the complex. After 1 h, desired coupling products were isolated in >88% yields for all aryl bromides which were screened. An isolated yield of 99% was obtained when electron-rich 2-bromoanisole was utilized as the reactant. Even sterically hindered 2-bromomesitylene underwent coupling to give the desired biphenyl product in 88% yield. The use of several different solvents and bases were explored with complex **5b** in an effort to enhance its performance under the reaction conditions. However, complex **5b** was unsuccessful in Suzuki−Miyaura CC coupling reactions utilizing aryl chlorides under a variety of conditions.

These studies showed that while complex **5b** was effective for coupling *p*-tolylboronic acid with aryl bromides, complex

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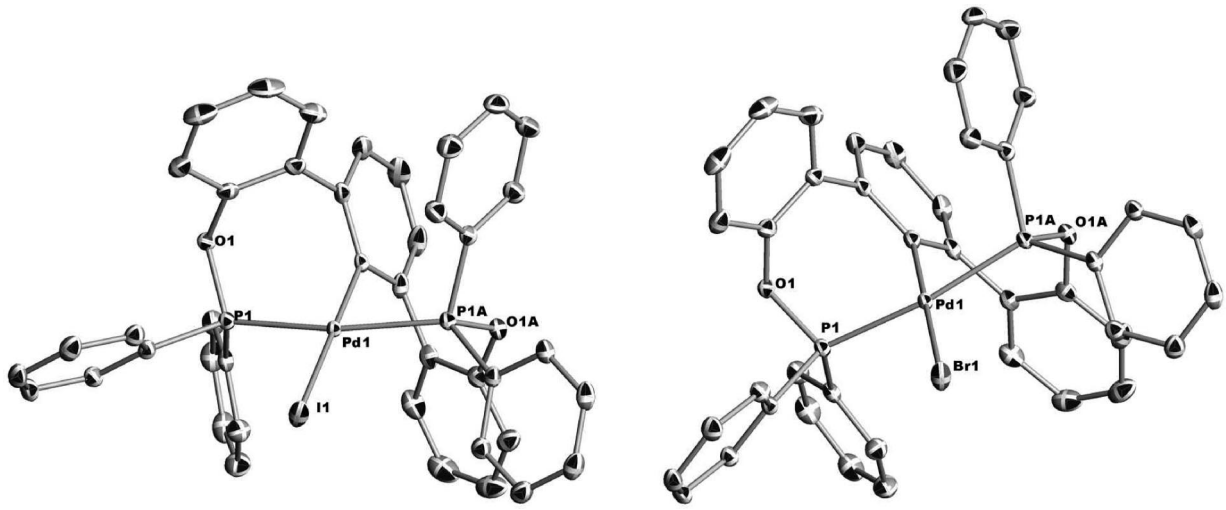


Figure 1. Ortep representations (50% probability ellipsoids) of the molecular structure of **5a** (left) and **5b** (right).

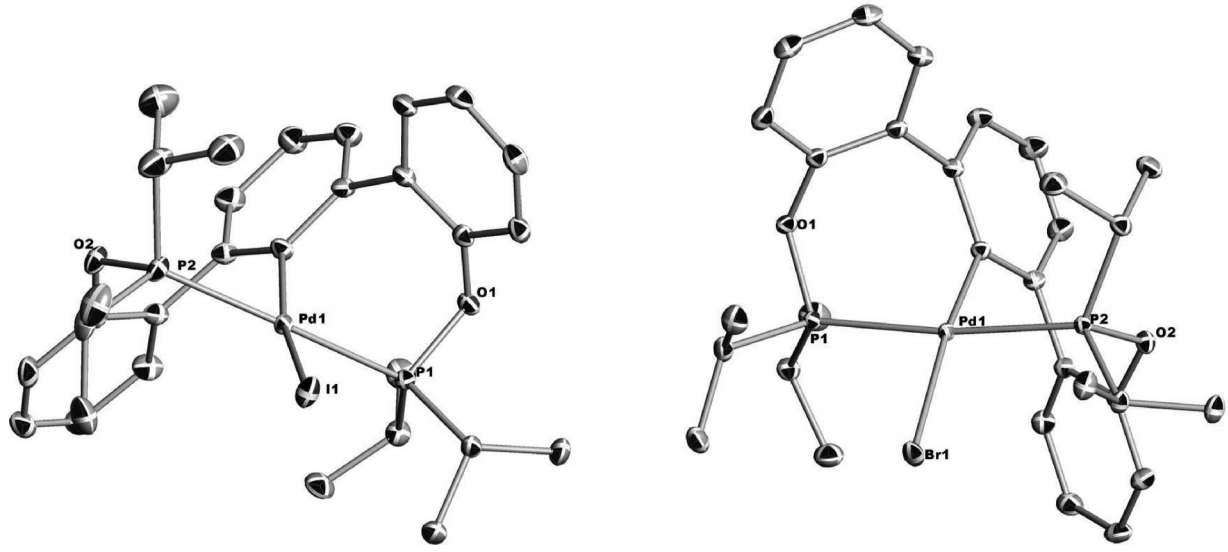
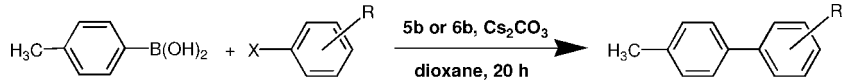


Figure 2. Ortep representations (50% probability ellipsoids) of the molecular structure of **6a** (left) and **6b** (right).

Table 1. Selected Bond Lengths and Angles

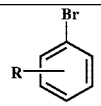
	7[50]	**5a**	**5b**[50]	**6a**	**6b**
Pd−C(1) (Å)	2.067(4)	2.058(2)	2.063(3)	2.053(2)	2.0442(14)
Pd−P(1) (Å)	2.3071(7)	2.2808(4)	2.2824(5)	2.3365(5)	2.3023(4)
Pd−P(2) (Å)	2.3071(7)	2.2808(4)	2.2824(5)	2.3026(5)	2.3271(4)
Pd−X(Å)	2.5024(5)	2.6408(3)	2.4918(4)	2.6689(2)	2.51449(18)
C(1)−Pd−X	180.0°	180.0°	180.0°	165.90(6)°	168.20(4)°
P(1)−Pd−P(2)	169.48(4)°	167.53°	167.41(3)°	172.393(19)°	172.772(14)°
Twist Angle Angle (Φ)	76.7°	73.9°	73.8°	66.8°	66.4°

Scheme 3. Suzuki−Miyaura CC Coupling Reactions



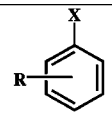
6b was shown to promote the CC coupling reaction of *p*-tolylboronic acid to either aryl bromides or aryl chlorides. Complex **6b** was chosen for a more thorough evaluation of its catalytic properties because of its superior performance. Several aryl bromides and aryl chlorides were used as substrates for coupling with *p*-tolylboronic acid (Table 3). Unless otherwise noted, 1 mol% of complex **6b** was used. Reactions were carried out at three different reaction temperatures in order to determine catalytic activity under a variety of conditions. In refluxing 1,4-dioxane, the coupling reaction proceeded in excellent yield for all substrates evaluated. The most noteworthy results are the coupling of the boronic acid with chloromesitylene in 86% yield and with 2-chloroanisole in 99% yield. Relatively few palladium complexes are capable of catalyzing the Suzuki−Miyaura reaction with sterically hindered or electron rich aryl chlorides.[15,17,60] Furthermore, these yields are, to our knowledge, among the highest attained using PCP pincer complexes in the Suzuki−Miyaura reaction with such sterically hindered or electron rich aryl chlorides.[49,60,61]

Table 2. Suzuki−Miyaura CC Coupling Reactions between Substituted Arylbromides and *p*-Tolylboronic Acid Promoted by 5b

 R =	X	mol% 5b	Temperature (°C)	Yield (%)[a]
H	Br	1	100	99
2-methoxy	Br	1	100	99
2,4,6-trimethyl	Br	1	100	88

[a] Isolated yield from 0.6 mmol aryl halide, 0.9 mmol *p*-tolylboronic acid, 1.8 mmol of Cs_2CO_3, 2 mL dioxane

Table 3. Suzuki−Miyaura CC Coupling Reactions between Substituted Arylhalides and *p*-Tolylboronic Acid Promoted by 6b

 R =	X	mol% 6b	Temperature (°C)	Yield (%)[a]
H	Br	1	100	96
H	Br	1	75	98
H	Br	1	50	76[b]
2-methyl	Br	1	100	98
2-methyl	Br	1	75	97
2-methyl	Br	1	50	45[b]
2-methoxy	Br	1	100	99
2-methoxy	Br	1	75	96
2-methoxy	Br	1	50	36
2,4,6-trimethyl	Br	1	100	87
2,4,6-trimethyl	Br	1	75	77[b]
2,4,6-trimethyl	Br	1	50	<10
H	Cl	1	100	89
H	Cl	1	75	68
H	Cl	2	75	79
2-methyl	Cl	1	100	93
2-methyl	Cl	1	75	61
2-methyl	Cl	2	75	62[b]
2-methoxy	Cl	1	100	99
2-methoxy	Cl	1	75	82
2-methoxy	Cl	2	75	83[b]
2-methoxy	Cl	0.5	75	52[b]
4-methoxy	Cl	1	75	81
4-methoxy	Cl	2	75	83
2,4,6-trimethyl	Cl	1	100	86
2,4,6-trimethyl	Cl	1	75	68
2,4,6-trimethyl	Cl	2	75	69[b]

[a] Isolated yield from 0.6 mmol aryl halide, 0.9 mmol *p*-tolylboronic acid, 1.8 mmol of Cs_2CO_3, 2 mL dioxane. [b] Analysis of reaction products by protocol described in text complicated by presence of other impurities, and thus ^{1}H NMR spectroscopy was used to correct yields.

The same reactions were run at 75 °C while all other conditions remained the same. Of the aryl bromides, only bromomesitylene gave a significant decrease in coupling yield at this temperature. The aryl chlorides, on the other hand, all had significantly reduced yields at 75 °C. Peculiarly, electron rich 2-chloroanisole and 4-chloroanisole gave respectable yields for biaryl formation. Increasing the catalyst loading to 2 mol%, however, gave a notable increase in yield only for chlorobenzene and 2-chlorotoluene. Even with these substrates, the increase in yield was only slightly more than 10%. It is quite notable that the coupling reaction occurred when using aryl chlorides at 75 °C since pincer complexes usually do not catalyze such reactions using unactivated chloroarenes at temperatures below 100 °C (vide infra), though reaction temperatures as low as room temperature have been achieved with other palladium complexes.[14,15,62] An additional test was run at 75 °C was done with 2-chloroanisole using only 0.5 mol% of **6b** which gave a yield of 52% and thus a turnover number of 104.

Complex **6b** was tested for catalytic activity at a reaction temperature of 50 °C while maintaining all other conditions. At this temperature, desired coupling was not observed for any of the aryl chlorides used. Optimization of the reaction conditions was attempted by utilizing alternative bases and even aryl trihydroxyborates[63] as reactants, but all efforts were unsuccessful in attaining coupling at 50 °C with aryl chlorides as substrates. While yields were depressed, aryl bromides, with the exception of bromomesitylene, were successfully coupled at 50 °C.

Two different reaction mechanisms are conceivable for the coupling of aryl halides and aryl boronic acids by palladium pincer complexes and other related palladacycles. In one mechanism, the complex releases colloidal Pd(0) which might serve as the active catalyst by a Pd(0)/Pd(II) catalytic cycle. In the other mechanism, the complex remains intact and catalysis occurs via a Pd(II)/Pd(IV) catalytic cycle. For the majority of palladacycles, evidence suggests that the Pd(0)/Pd(II) catalytic cycle is followed.[64−68] There have been, however, a small number of pincer complexes reported for which mechanistic tests suggest a Pd(II)/Pd(IV) catalytic cycle.[49]

Observations on these catalysis reactions are consistent with a classical Pd(0)/Pd(II) catalytic cycle. Reaction mixtures begin turning yellow fairly soon after being heated in an oil bath. At 100 °C, color changes became evident within about 1 min. After reacting for 20 h, black precipitates were also clearly evident. At 75 °C, similar colorations developed more slowly and were apparent within 5 min. Similar black precipitates were also evident after 20 h. Reaction mixtures involving aryl chlorides at 50 °C slowly turned yellow, but no black precipitate was evident. When using aryl bromides at 50 °C, the reactions slowly turned yellow and some black precipitate was evident after 20 h.

As the more successful CC coupling reactions were also accompanied by the visual indicators often attributed to the formation of elemental palladium, it seems reasonable to ascribe the efficacy of compound **6b** to its ability to release Pd(0) in a beneficial way. A more definitive analysis involves using elemental mercury to amalgamate released palladium to remove participation of Pd(0) in the catalytic cycle.[66−71] Catalytic CC coupling reactions between 2-chloroanisole or chlorobenzene with *p*-tolylboronic acid at 75 °C were thus attempted in the presence of a drop (ca. 120 mg) of mercury (99.999% purity). Analysis of such reaction mixtures showed no CC coupling product, indicating that the catalytic activity of complex **6b** is

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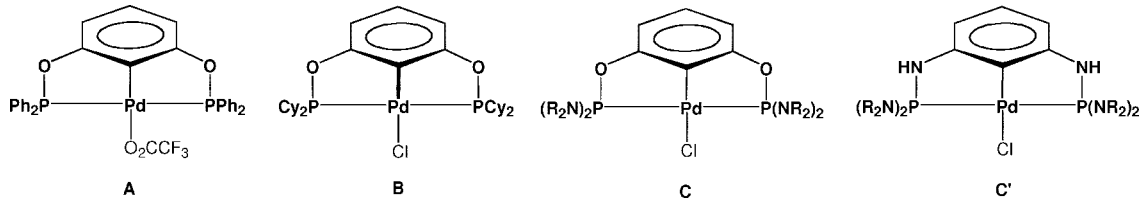
Chart 2



coupled somehow to the formation of colloidal Pd(0).[68] Heating (75 °C) solutions of **6b** alone or in the presence of mercury in dioxane for extended periods of time (16 h) provided no evidence of decomposition, attesting to the inherit thermal robustness of the compound. Solutions of **6b** heated in the presence of Cs_2CO_3, or a mixture of Cs_2CO_3 and Hg, however, became yellow colored and gave new species as indicated by the presence of new ^{31}P NMR signals (62.2 and 52.6 ppm, respectively). These new resonances might suggest the presence of $^{i}Pr_2P(=O)OAr$ functionalities[72] and oxidation of the ligand system in **6b**. One of several possible transformations of palladium phosphinite ligands involves hydrolysis.[73] At this time a fuller picture of the process leading to collodial Pd(0) is not available, due to the obvious complexity of the reagents and additives all playing possible roles in transforming the precatalyst **6b** into its active form.

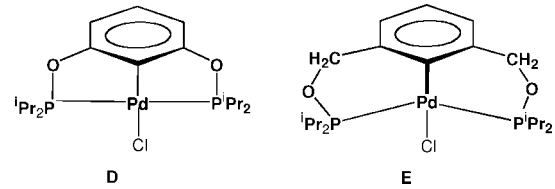
Regardless of mechanism, complex **6b** displays noteworthy activity as a precatalyst. Comparisons to some recent work on PCP diphosphinite pincer complexes (Chart 2) can be made. Complex **A** has shown good activity for promoting the coupling of bromobenzenes with phenyl boronic acid, but is only able to achieve effective conversions with the activated chloroarene, 4-chloronitrobenzene.[59] The closely related derivative **B** was also reported to utilize 4-chloronitrobenzene in coupling with phenylboronic acid at only 40 °C, albeit it at very low conversions (9−12%).[74] Compounds **C** and **C′** (NR_2 = piperidinyl) display impressive activities, and can couple even unactivated chloroarenes with phenylboronic acid with both high efficiency and rates at 100 °C.[49] This system is very interesting because no evidence for the participation of colloidal palladium was found, for example, by the lack of impact on catalysis by the addition of mercury.

The activity of complex **6b** might be attributed to the differently sized chelate rings, having 7 atoms versus 5 (see examples in Chart 2). It has been recently reported that in the Heck reaction involving the olefination of haloarenes, PCP pincer complex **E** outperforms complex **D** (Chart 3) and has a greater range of accessible substrates.[75,76]

Conclusion

We have synthesized four diphosphinite palladium pincer complexes based on a *m*-terphenyl framework. The synthesis of the pincer ligands and complexes was accomplished using standard methods for the synthesis of diphosphinite pincer complexes. Single crystal X-ray diffraction methods were used to analyze the structures of these complexes. Complexes **5b** and **6b** were evaluated for their catalytic activity in the Suzuki−Miyaura coupling reaction between 4-tolylboronic acid and a variety of aryl halides. Complex **5b** proved to be excellent for promoting the CC coupling of 4-tolylboronic acid with aryl bromides, including bromomesitylene. Complex **6b** had even higher catalytic activity as it successfully promoted the CC coupling of the boronic acid with aryl chlorides in high yield and even at reduced temperatures. Mechanistic investigations using elemental mercury suggest that these pincer complexes may ultimately serve as precursors for the release of highly active colloidal Pd(0) as the actual catalytic species.

Chart 3



Experimental Section

General Procedures. All reactions, unless otherwise stated, were carried out utilizing Schlenk techniques or in an MBRAUN Labmaster 130 drybox under an atmosphere of dry N_2. Tetrahydrofuran (THF), diethyl ether, hexanes and *n*-pentane were purified prior to use by distillation from sodium/benzophenone ketyl under an atmosphere of dry N_2. Benzene (anhydrous) and toluene (Anhydrous, 99.9%) were purchased from Acros and used as received. Methylene chloride was passed through alumina and degassed prior to use. 1,4-Dioxane was dried over 4 Å molecular sieves and degassed immediately prior to use. Diphenylchlorophosphine (95% tech.) and diisopropylchlorophosphine (97%) were purchased from Acros and used without further purification. *para*-Tolylboronic acid was synthesized according to a literature procedure[77] and was purified by recrystallization from H_2O or by repeated rinsing with hexanes.

NMR data were recorded on a Varian Inova spectrometer operating at 400, 100, and 161.8 MHz for the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra, respectively, unless otherwise stated. $^{31}P\{^1H\}$ NMR data are referenced to an external 85% H_3PO_4 standard, while the ^1H and $^{13}C\{^1H\}$ NMR data are referenced using residual solvent signals.

2,6-(2-$CH_3OC_6H_4$)$_2C_6H_3I$ (1a). A round-bottom flask was equipped with a reflux condenser and charged with a stirbar before the addition of 200 mL of THF. 1,3-Dichlorobenzene (5.00 g, 34.0 mmol) was added via syringe and the contents were cooled to −78 °C. With rapid stirring, *n*-BuLi (16.3 mL, 40.8 mmol) was added dropwise via syringe over 30 min during which the clear solution turned milky white in color. The contents were stirred at −78 °C for 2 h. To this was added a solution of 2-methoxyphenylmagnesium bromide (freshly prepared from 2-bromoanisole (22.3 g, 119 mmol)

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Table 4. Selected Data Collection and Structure Solution Information

compound	**5a**	**5b**	**6a**	**6b**
Empirical formula	$C_{42}H_{31}IO_2P_2Pd$	$C_{42}H_{31}BrO_2P_2Pd$	$C_{30}H_{39}IO_2P_2Pd$	$C_{30}H_{39}BrO_2P_2Pd$
Formula weight	862.91	815.92	726.85	679.86
Temperature (K)	100	100	100	100[a]
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbcn*	*Pbcn*	*P*2(1)/*n*	*P*2(1)/*n*
Unit cell dimensions	$a = 15.1802(5)$	$a = 14.9444(2)$	$a = 9.1944(3)$	$a = 9.2586(1)$
	$b = 11.6483(3)$	$b = 11.6289(2)$	$b = 16.2698(5)$	$b = 16.0146(2)$
	$c = 19.6981(6)$	$c = 19.7745(3)$	$c = 19.5100(6)$	$c = 19.3448(3)$
	$\alpha = 90$	$\alpha = 90$	$\alpha = 90$	$\alpha = 90$
	$\beta = 90$	$\beta = 90$	$\beta = 94.999(1)$	$\beta = 95.296(1)$
	$\gamma = 90$	$\gamma = 90$	$\gamma = 90$	$\gamma = 90$
Volume (Å^3)	3483.1(2)	3436.55(9)	2907.4(2)	2856.06(6)
Z	4	4	4	4
Density (calcd. g/cm^3)	1.646	1.577	1.661	1.581
Absorption coeff. (mm^{-1})	1.548	1.833	1.836	2.187
F(000)	1712	1640	1456	1384
Crystal size (mm)	0.58 × 0.40 × 0.10	0.26 × 0.20 × 0.12	0.40 × 0.20 × 0.10	0.35 × 0.35 × 0.20
Crystal color and shape	Lt. brown plate	Lt. brown block	Lt. yellow block	Lt. yellow block
θ range data collection	2.71∼33.17	3.03∼33.14	1.63∼28.32	1.65∼27.5
Limiting indices	$-23 < h < 23$	$-22 < h < 10$	$-12 < h < 12$	$-12 < h < 12$
	$-17 < k < 16$	$-8 < k < 17$	$-21 < k < 21$	$-20 < k < 16$
	$-30 < l < 30$	$-30 < l < 23$	$-25 < l < 25$	$-25 < l < 20$
Reflections collected	78927	11657	48996	29738
Independent reflections	6639	6006	7198	6546
Refinement method	Full-matrix least-squares on F^2			
Data/restraints/parameters	78927/0/236	11657/0/235	48996/0/333	29738/0/333
Goodness-of-fit on F^2	1.150	1.018	1.102	1.068
Final *R* indices $[I > 2\sigma(I)]^{a,b}$	$R1 = 0.0288$	$R1 = 0.0362$	$R1 = 0.0228$	$R1 = 0.0173$
	$wR2 = 0.0594$	$wR2 = 0.0774$	$wR2 = 0.0542$	$wR2 = 0.0430$
R indices (all data)	$R1 = 0.0465$	$R1 = 0.0677$	$R1 = 0.0239$	$R1 = 0.0190$
	$wR2 = 0.0720$	$wR2 = 0.0885$	$wR2 = 0.0550$	$wR2 = 0.0454$

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_W(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program.

and Mg (4.96 g, 20.4 mmol) in 150 mL THF). The resulting solution was then warmed to room temperature before heating under reflux overnight. The contents were cooled to 0 °C before the addition of excess iodine (15.6 g, 61.5 mmol) which was added in portions under positive pressure of N_2. The mixture with iodine was stirred for 1 h. The contents were then poured into an aqueous Na_2SO_3 solution (5% by weight). The organics were extracted with diethyl ether, washed with 5% Na_2SO_3 (1 × 100 mL), brine (3 × 100 mL), collected and dried over $MgSO_4$. Rotary evaporation yielded an off-white solid which was recrystallized from ethanol to give 8.94 g (63%) of white solid. (Chemical shifts of two isomers are reported without further assigning to *syn*- or *anti*-) ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.81−3.83 (s, 6H), 6.97−7.00 (d, 2H, $J = 8$ Hz), 7.03−7.08 (t, 2H, $J = 8$ Hz), 7.17−7.27 (m, 4H), 7.38−7.46 (m, 3H).

2,6-(2-$CH_3OC_6H_4$)$_2$$C_6H_3$Br (1b). Compound **1b** was synthesized in a manner analogous to that outlined for **1a**. The 2,6-dichlorophenyllithium solution was prepared from 6.47 g of 1,3-dichlorobenzene (44.0 mmol) and 21.1 mL of *n*-BuLi (52.8 mmol) in 200 mL of THF. To this was added a freshly prepared solution of the Grignard reagent (prepared from 2-bromoanisole (28.8 g, 154 mmol) and Mg (6.42 g, 264 mmol) in 200 mL THF). After heating under reflux overnight, bromine (3.10 mL, 60.5 mmol) was added slowly via syringe. The crude product was obtained as for compound **1a**. Purification was accomplished by rinsing with *n*-pentane to yield 9.89 g (61%) of **1b** as a white powder. (Chemical shifts of two isomers are reported without further assigning to *syn*- or *anti*-) ^{1}H NMR ($CDCl_3$): δ 3.80−3.82 (s, 6H), 6.98−7.00 (d, 2H, $J = 8$ Hz), 7.04−7.05 (t, 2H, $J = 8$ Hz), 7.26 (t, 2H, $J = 8$ Hz), 7.27 (d, 2H, $J = 8$ Hz), 7.37−7.41 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 55.61, 55.66, 110.91, 111.05, 120.21, 120.27, 126.45, 126.57, 129.12, 130.13, 130.22, 130.75, 131.02, 131.12, 131.27, 140.292, 156.57, 156.71. Elemental analysis calculated for $C_{20}H_{17}O_2Br$: C, 65.05; H, 4.65. Found: C, 64.81; H, 4.70.

2,6-(2-HOC_6H_4)$_2$$C_6H_3$I (2a). A round-bottom flask was charged with a stirbar, **1a** (2.00 g, 4.81 mmol), and CH_2Cl_2 (100 mL). The flask was equipped with a reflux condenser. A 1.0 M solution of BBr_3 (9.61 mL, 9.61 mmol) was added dropwise via syringe. The contents were then heated under reflux for 2 h. The solution turned slightly pink in color during this time. The solution was then cooled to room temperature and 3 mL concentrated HCl was slowly added via syringe with rapid stirring. The volatiles were removed via rotary evaporation to yield a pale yellow residue. This was taken up in 100 mL of ethyl acetate and filtered through a pad of silica gel. The filtrate was concentrated via rotary evaporation to yield a light orange solid. The crude solid was taken up in 5 mL CH_2Cl_2 and precipitated into hexanes. The precipitate was isolated by filtration, rinsed with hexanes and dried *in vacuo* to yield **2a** as a pale tan solid (1.64 g, 88%). mp 120−122 °C. (Chemical shifts of two isomers are reported without further assigning to *syn*- or *anti*-) ^{1}H NMR ($CDCl_3$): δ 4.75 (broad s, 2H), 6.90 (d, 1H, $J = 8$ Hz), 6.97−7.02 (m, 3H), 7.09−7.15 (m, 2H), 7.24−7.53 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 107.6, 115.98, 116.00, 120.63, 120.67, 128.64, 129.00, 129.68, 129.95, 130.15, 130.21, 130.53, 131.81, 132.18, 143.65, 144.04, 151.98, 152.19.

2,6-(2-HOC_6H_4)$_2$$C_6H_3$Br (2b). Compound **2b** was synthesized and purified by a method analogous to that outlined for compound **2a**. The following quantities of starting materials were used: 4.00 g (10.8 mmol) **1b**, 21.7 mL (21.7 mmol) 1.0 M BBr_3 in CH_2Cl_2, and 75 mL CH_2Cl_2. Compound **2b** was isolated as a light tan solid (3.32 g, 90%). mp 134−136 °C. (Chemical shifts of two isomers are reported without further assigning to *syn*- or *anti*-) ^{1}H NMR ($CDCl_3$): δ 4.94 (broad s, 2H), 6.94 (d, 1H, $J = 8$ Hz), 6.99−7.05 (m, 3H), 7.17−7.22 (m, 2H), 7.28−7.51 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$): 115.93, 120.66, 126.71, 127.74, 128.10, 128.22, 128.60, 129.66, 129.89, 130.35, 130.66, 131.50, 131.86, 139.42, 139.57, 152.29, 152.45.

2,6-(2-$Ph_2POC_6H_4$)$_2C_6H_3I$ (3a). A three-neck round-bottom flask was charged with a stirbar and **2a** (0.325 g, 0.837 mmol) before being equipped with a reflux condenser. To this was added anhydrous toluene (40 mL) followed by chlorodiphenylphosphine (0.30 mL, 1.63 mmol). A pale yellow color was evident upon adding the chlorodiphenylphosphine. Excess triethylamine (0.36 mL, 2.51 mmol) was added and the solution became cloudy and pale pink in color. The contents were heated to reflux and the solution became homogeneous. After 3 h, a white precipitate had formed. A small aliquot was collected via syringe and concentrated *in vacuo* for $^{31}P\{^1H\}$ and ^1H NMR analysis, which demonstrated complete consumption of the starting material by disappearance of the resonance assigned to the hydroxyl groups of **2a** in the ^1H NMR. The contents were cooled to room temperature. The solution was filtered through a thin pad of Celite in a dry box. The Celite was rinsed with additional toluene (2 × 10 mL). The combined organics were concentrated *in vacuo*, yielding a sticky yellow solid. The solid was dissolved in 10 mL of diethyl ether, filtered through Celite, and dried *in vacuo* to yield the desired diphosphinite ligand, **3a**, as a pale-yellow solid, which was not purified further (0.522 g, 82%). (Chemical shifts of two isomers are reported without further assigning to *syn*- or *anti*-) ^1H NMR ($CDCl_3$): δ 6.98 (d, 2H, J = 8 Hz), 7.07 (t, 1H, J = 4 Hz), 7.11 (d, 2H, J = 8 Hz), 7.23 (d, 2H, J = 8 Hz), 7.26−7.34 (broad m, 20H), 7.38 (t, 4H, J = 4 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 111.8.

2,6-(2-$Ph_2POC_6H_4$)$_2C_6H_3Br$ (3b). Compound **3b** was synthesized and purified by a method analogous to that outlined for compound **3a**. The following quantities of starting materials were used: 0.500 mg (1.47 mmol) **2b**, 0.53 mL (2.87 mmol) chlorodiphenylphosphine, 0.36 mL (2.51 mmol) triethylamine, and 40 mL of anhydrous toluene. Compound **3b** was isolated as a pale-tan, sticky solid, which was not purified further (0.800 g, 77%). (Chemical shifts of two isomers are reported without further assigning to *syn*- or *anti*-) ^1H NMR ($CDCl_3$): δ 7.01 (d, 2H, J = 8 Hz), 7.08 (t, 1H, J = 4 Hz), 7.11 (d, 2H, J = 8 Hz), 7.24−7.34 (broad m, 22H), 7.38 (t, 4H, J = 4 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 111.8.

2,6-(2-^{i}Pr$_2$POC$_6$H$_4$)$_2$C$_6$H$_3$I (4a). A three-neck round-bottom flask was charged with a stirbar and **2a** (0.300 g, 0.773 mmol) before being equipped with a reflux condenser. To this was added anhydrous toluene (30 mL) followed by chlorodiisopropylphosphine (0.24 mL, 1.5 mmol) which resulted in a light pink solution. Triethylamine (0.33 mL, 2.3 mmol) was then added, resulting in cloudiness that dissipated within 5 min. The contents were heated to reflux and the solution became homogeneous and clear after 30 min. After heating under reflux for 20 h, the contents were cooled to room temperature. A small aliquot was collected via syringe and concentrated *in vacuo* for $^{31}P\{^1H\}$ and ^1H NMR analysis, which demonstrated complete consumption of the starting material by disappearance of the resonance assigned to the hydroxyl groups of **2a** in the ^1H NMR. Degassed petroleum ether (10 mL) was added and a white precipitate was evident after a few minutes of stirring. The contents were taken into the dry box and filtered through Celite. The filtrate was concentrated *in vacuo*, yielding a pale-brown oil, which was not purified further (0.308 g, 64%). (Chemical shifts of two isomers are reported without further assigning to *syn*- or *anti*-) ^1H NMR ($CDCl_3$, 300 MHz): δ 0.86−1.02 (m, 18H), 0.99−1.26 (m,6H), 1.61−1.84 (m, 4H), 7.02 (t, 2H, J = 8 Hz), 7.12−7.15 (m, 2H), 7.20 (d, 2H, J = 8 Hz), 7.30−7.38 (m, 4H), 7.49 (t, 1H, J = 8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 146.7.

2,6-(2-^{i}Pr$_2$POC$_6$H$_4$)$_2$C$_6$H$_3$Br (4b). Compound **4b** was synthesized and purified by a method analogous to that outlined for compound **4a**. The following quantities of starting materials were used: 0.200 g (0.586 mmol) **2b**, 0.18 mL (1.14 mmol) of chlorodiisopropylphosphine, 0.25 mL (1.76 mmol) triethylamine, and 30 mL of anhydrous toluene. Compound **4b** was isolated as a pale-yellow oil, which was not purified further (0.289 g, 86%). (Chemical shifts of two isomers are reported without further assigning to *syn*- or *anti*-) ^1H NMR ($CDCl_3$): δ 0.87−1.05 (m, 18H), 1.16−1.31 (m,6H), 1.66−1.72 (m, 2H), 1.76−1.82 (m, 2H), 7.02 (t, 2H, J = 8 Hz), 7.11−7.14 (m, 2H), 7.20 (d, 2H, J = 8 Hz), 7.30−7.38 (m, 4H), 7.47−7.51 (t, 1H, J = 8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 146.9.

2,6-(2-$Ph_2POC_6H_4$)$_2C_6H_3PdI$ (5a). A flame dried, 20 mL screw cap vial was charged with a stir bar, **3a** (0.085 g, 0.11 mmol), and 0.051 g (0.056 mmol) Pd_2dba_3. Anhydrous benzene (5 mL) was added and the vial was sealed. The contents were stirred at room temperature and the reaction was monitored by ^{31}P NMR analysis. After 1 h, complete consumption of the free ligand was shown by the disappearance of its ^{31}P NMR resonance. The dark- purple solution was filtered through Celite. The resulting orange solution was concentrated via rotary evaporation to yield a pale orange solid. The crude product was purified by flash chromatography over silica gel. Dibenzylideneacetone was eluted first with 10% EtOAc/hexanes followed by **5a** which was eluted with chloroform. Rotary evaporation of the chloroform gave a pale orange solid which was rinsed with 5 mL diethyl ether, filtered and dried *in vacuo* to yield analytically pure **5a** as a pale-orange solid (0.077 g, 79%). X-ray quality crystals were grown from vapor diffusion of hexanes into a concentrated chloroform solution at −5 °C. ^1H NMR ($CDCl_3$): δ 6.21 (d, 2H, J = 8 Hz), 6.76 (d, 2H, J = 8 Hz), 6.81 (d, 2H, J = 8 Hz), 7.01 (t, 2H, J = 8 Hz), 7.04 (t, 1H, J = 8 Hz), 7.17−7.20 (m, 6H), 7.26−7.29 (m, 4H), 7.35−7.44 (m, 8H), 7.68−7.73 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 121.6, 124.9, 125.2, 127.7 (virtual triplet, J = 5 Hz), 128.1 (virtual triplet, J = 5 Hz), 128.8, 128.9 (virtual triplet, J = 7 Hz), 130.1, 130.8, 131.4, 133.0 (virtual triplet, J = 7 Hz), 134.4 (virtual triplet, J = 22 Hz), 135.7, 143.2, 146.0, 151.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 118.2. Elemental analysis calcd for $C_{42}H_{31}O_2P_2PdI$: C, 58.46; H, 3.62. Found: C, 58.19; H, 3.65.

2,6-(2-$Ph_2POC_6H_4$)$_2C_6H_3PdBr$ (5b). Complex **5b** was synthesized and purified by a method analogous to that outlined for complex **5a**. The following quantities of starting materials were used: 0.145 g (0.204 mmol) of **3b**, 0.093 g (0.102 mmol) Pd_2dba_3, and 10 mL of anhydrous benzene. Analytically pure **5b** was isolated as an off-white solid (0.1177 g, 70%). X-ray quality crystals were grown from vapor diffusion of hexanes into a concentrated chloroform solution at −5 °C. ^1H NMR ($CDCl_3$): δ 6.18 (d, 2H, J = 8 Hz), 6.75 (d, 2H, J = 8 Hz), 6.80 (d, 2H, J = 8 Hz), 6.99 (t, 2H, J = 8 Hz), 7.22 (t, 1H, J = 8 Hz), 7.14−7.16 (m, 6H), 7.26−7.29 (m, 4H), 7.35−7.46 (m, 8H), 7.72−7.77 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 121.6, 124.8, 125.1, 127.7 (virtual triplet, J = 5 Hz), 128.0 (virtual triplet, J = 5 Hz), 128.8 (virtual triplet, J = 7 Hz), 130.1, 131.3, 132.9 (virtual triplet, J = 7 Hz), 133.3, 133.6, 134.2 (virtual triplet, J = 22 Hz), 135.6, 143.1, 145.9, 151.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 118.2. Elemental analysis calculated for $C_{42}H_{31}O_2P_2PdBr$: C, 61.82; H, 3.83. Found: C, 61.07; H, 3.78.

2,6-(2-^{i}Pr$_2$POC$_6$H$_4$)$_2$C$_6$H$_3$PdI (6a). A flame dried, 20 mL screw cap vial was charged with stir bar, **4a** (0.160 g, 0.258 mmol), and 0.5 equivalents of Pd_2dba_3 (0.118 g, 0.129 mmol). Anhydrous benzene (15 mL) was then added and the vial was sealed. The contents were stirred at room temperature and the reaction was monitored by $^{31}P\{^1H\}$ NMR analysis. After 20 h, $^{31}P\{^1H\}$ NMR analysis showed the disappearance of the resonance of the free ligand. The solution was filtered and solvent was removed from the filtrate via rotary evaporation to yield a pale yellow solid. The crude product was purified by flash chromatography over silica gel (EtOAc:hexanes, 1:10). The product after evaporation of volatiles was rinsed with 5 mL diethyl ether, filtered and dried *in vacuo* to yield analytically pure **6a** as a light-orange solid (0.120 g, 64%). X-ray quality crystals were grown from vapor diffusion of hexanes into a concentrated chloroform solution at −5 °C. ^1H NMR ($CDCl_3$): δ 0.64−0.70 (m, 6H), 1.00−1.06 (m, 6H), 1.24−1.29 (m, 6H), 1.40−1.45 (m, 6H), 2.18−2.24 (m, 2H), 3.28−3.32 (m, 2H), 6.99 (d, 2H, J = 8 Hz), 7.07 (d, 2H, J= 8 Hz), 7.16 (t, 1H, J = 8 Hz), 7.21 (t, 2H, J = 8 Hz), 7.26−7.33 (m, 4H). $^{31}P\{^1H\}$ NMR ($CDCl_3$):

δ 153.3. Elemental analysis calcd for $C_{30}H_{39}O_2P_2PdI$: C, 49.57; H, 5.41. Found: C, 49.63; H, 5.53.

2,6-[2-OP(^{i}Pr)$_2$C$_6$H$_4$]$_2$C$_6$H$_3$PdBr (6b). Complex **6b** was synthesized and purified by a method analogous to that outlined for complex **6a**. The following quantities of starting materials were used: 0.285 g (0.497 mmol) **4b**, 0.228 g (0.249 mmol) Pd_2dba_3, and 10 mL of anhydrous benzene. Analytically pure **6b** was isolated as a white solid (0.192 g, 57%). X-ray quality crystals were grown from vapor diffusion of hexanes into a concentrated chloroform solution at −5 °C. ^{1}H NMR ($CDCl_3$): δ 0.65−0.71 (m, 6H), 0.98−1.04 (m, 6H), 1.26−1.32 (m, 6H), 1.40−1.45 (m, 6H), 2.13−2.19 (m, 2H), 3.04−3.11 (m, 2H), 6.98 (d, 2H, J = 8 Hz), 7.08 (d, 2H, J= 8 Hz), 7.14 (t, 1H, J = 8 Hz), 7.21 (t, 2H, J = 8 Hz), 7.26−7.33 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.4, 16.6, 17.3 (virtual triplet, J = 5 Hz), 18.5, 27.4 (virtual triplet, J = 14 Hz), 29.9 (virtual triplet, J = 10 Hz), 122.1, 124.5, 124.9, 128.0, 129.3, 132.1, 136.6, 142.9, 144.2, 152.2. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 152.6. Elemental analysis calcd for $C_{30}H_{39}O_2P_2PdBr$: C, 52.98; H, 5.78. Found: C, 52.58; H, 5.76.

Typical Procedure for Suzuki−Miyaura CC Coupling Reactions. A 5 mL conical vial was charged with Cs_2CO_3 (0.586 g, 1.8 mmol), *p*-tolylboronic acid (0.122 g, 0.9 mmol), 0.6 mmol of aryl halide, and 1 mol% of either complex **5b** or **6b**. The vial was equipped with a magnetic spinvane and a reflux condenser before being filled with nitrogen. 1,4-Dioxane (2 mL) was added and the vial placed in an oil bath maintained at the desired reaction temperature. After 20 h the reaction was cooled to room temperature, diluted with diethyl ether, and filtered through a thin pad of silica gel. The silica gel was rinsed with 25 mL of additional diethyl ether. The combined organics were concentrated under reduced pressure to yield the desired coupling product, typically of >95% purity as judged by ^{1}H NMR spectroscopy.

X-Ray Crystallographic Studies. The X-ray intensity data were measured at 100 K on a Bruker SMART Apex II CCD-based X-ray diffractometers system equipped with a Mo-target X-ray tubes (λ = 0.71073 Å) located at either Bruker AXS in Madison WI, (compounds **5a** and **5b**) or at Case Western Reserve University (compounds **6a** and **6b**). Data collection and solution parameters are summarized in Table 4. Further information is provided within the cif files supplied as Supporting Information. Crystals were mounted on a MiTeGen micromount using paratone-N which were then frozen. The frames were integrated with the Bruker SAINT build in APEX II software package using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using AXScale. The structures were solved and refined using the Bruker SHELXTL (Version 6.14) software. The positions of all non-hydrogen atoms were derived from the Direct Methods (TREF) solution. With all non-hydrogen atoms being anisotropic and all hydrogen atoms being isotropic the structure was refined to convergence by least-squares method on F^2, XSHELL (Version 6.3.1), incorporated in SHELXTL (Version 6.14).

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Supporting Information Available: CIF files having full X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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