

New PCN and PCP Pincer Palladium(II) Complexes: Convenient Synthesis via Facile One-Pot Phosphorylation/Palladation Reaction and Structural Characterization

Jun-Fang Gong, Yan-Hui Zhang, Mao-Ping Song,* and Chen Xu

Department of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Zhengzhou University, Zhengzhou 450052, People's Republic of China

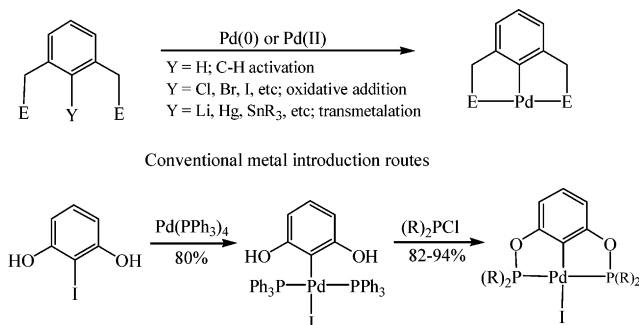
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A series of new PCN pincer palladium(II) complexes with phosphinito group **2a–d** and **3** were conveniently prepared via facile one-pot phosphorylation/palladation reaction of pyrazolyl or amino-containing *m*-phenol derivatives with chlorophosphines and PdCl₂. Two PCP pincer complexes **4a,b** were also readily obtained from resorcinol in an analogous yet simplified manner. All of the new complexes have been fully characterized by ¹H NMR, ¹³C{¹H} NMR, ³¹P{¹H} NMR, IR, ESI-MS, and elemental analysis. Additionally, the molecular structures of **2a–d** have been determined by X-ray single-crystal diffraction.

Introduction

Pincer palladium complexes containing anionic six-electron donor ligands of the type YCY have received a considerable amount of interest, primarily due to their feasible structural modifications with multiple choices of donor atoms and substituents thereon (Y = NR₂, SR, PR₂, OPR₂, etc.), high stability, and remarkable catalytic activities in various C–C coupling reactions.¹ The most common pincer palladacycles are NCN,² PCP,³ or SCS⁴ types, which are symmetrical with two identical donor groups and two equivalent five-membered palladacycles. It is generally accepted that the nature of the donor group greatly influences the reactivity, stability, and catalytic performances of these compounds. For instance, the hardness of the chelating N donor versus the softness of P donor results in the more labile N–Pd coordination and very different behavior of the corresponding NCN- and PCP-based complexes. Therefore, it can be anticipated that mixed, nonsymmetrical YCY' pincer palladium complexes, especially those containing potentially hemilabile hybrid PCN ligands, could benefit from advantages of varied donors and provide unique reactivity. By contrast, there are very few reports on the synthesis and applications of PCN pincer palladium complexes. This is partly

Scheme 1. Synthetic Strategy for Pincer Palladium Complexes



Uozumi's ligand introduction route for the synthesis of PCP pincer palladium complexes

because their preparation is a considerable challenge, which is laborious and requires a series of steps to introduce different donors. The synthesis of pincer palladium complexes is usually performed by direct palladation of the aryl ring via C–H

* To whom correspondence should be addressed. Tel.: +86 371 67763207. Fax: +86 371 67766667. E-mail: mpsong9350@zzu.edu.cn.

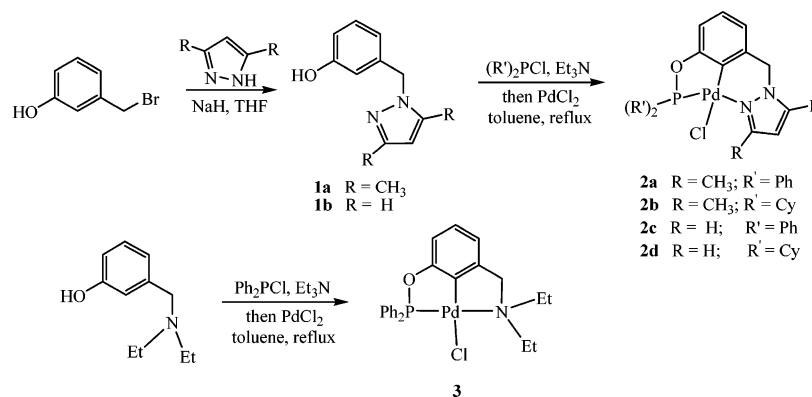
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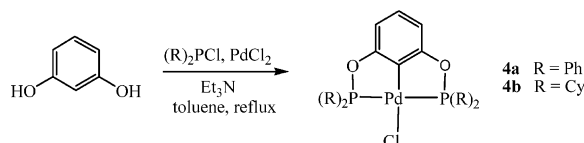
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Scheme 2. Synthesis of PCN Pincer Palladium Complexes 2a–d and 3



Scheme 3. Synthesis of PCP Pincer Palladium Complexes 4



activation, transmetalation reactions from aryllithium, arylmercury, or arylstannyl derivatives, or by oxidative addition of aryl halide onto Pd(0) precursors (Scheme 1). These methods were ascribed to metal introduction routes by Uozumi et al. because all of them must involve a palladation reaction of the corresponding pincer ligands creating a new Pd–C σ bond in the final step. Among these methods, the direct palladation protocol is particularly attractive because it does not require prefunctionalization of the pincer ligands to achieve regioselective metalation. Recently, Uozumi et al. developed a new synthetic strategy, which they called ligand introduction route in comparison to the former methods. In this ligand introduction method, the metal was introduced to the aromatic ring prior to the construction of the ligand unit. Novel NCN and PCP pincer palladium complexes with bulky, sterically demanding groups^{2d,e} or moisture-sensitive imino^{2f} and phosphinito groups,^{3j} which were difficult to synthesize via conventional metal introduction routes, were successfully synthesized.

Among the few examples of PCN pincer palladium complexes, Dupont et al. reported some PCN palladacycles where C donors were vinyl instead of aryl carbon anions by chloropalladation of heterosubstituted alkynes and used them in the Heck and Suzuki reactions.⁵ One of such compounds that contained a phosphinito and amino group was demonstrated to be highly efficient for the coupling of arylboronic acids and aryl chlorides. Additionally, Motoyama et al. prepared the first non-symmetrical PCN chiral pincer palladium complexes with (oxazolonyl)phenyl phosphinito ligands via oxidative addition of an appropriate bromo-substituted derivative.⁶ Herein, we wish to report a series of new PCN pincer palladium complexes that feature a phenyl backbone, a phosphinito group, and a pyrazolyl or amino group. These complexes were conveniently synthesized via a facile one-pot phosphorylation/palladation reaction of pyrazolyl or amino-containing *m*-phenol derivatives (Scheme 2). Two PCP complexes having two phosphinito groups were

produced in a similar yet simplified way (Scheme 3). All of the complexes obtained were applied to the Suzuki reactions of aryl halides and phenylboronic acid.

Results and Discussion

Synthesis of PCN and PCP Pincer Palladium Complexes.

The synthetic routes of PCN complexes 2 and 3 and PCP complexes 4 are demonstrated in Schemes 2 and 3, respectively. Nucleophilic substitution of 3-hydroxybenzyl bromide with pyrazole, 3,5-dimethylpyrazole, or diethylamine readily afforded pyrazolyl or amino-containing *m*-phenol derivatives, which reacted with diphenylchlorophosphine or dicyclohexylchlorophosphine in the presence of triethylamine in refluxing toluene for 6 h, followed by the addition of palladium chloride and reflux for another 18 h. The new PCN pincer palladium complexes 2 and 3 were successfully obtained in 54–72% isolated yields as white solids after chromatography on silica gel. Encouraged by the successful preparation of these complexes, we were interested to see whether those PCP complexes having two phosphinito groups could be synthesized by using this facile one-pot phosphorylation/palladation reaction. To simplify the procedure, resorcinol, the appropriate chlorophosphine, palladium chloride, as well as triethylamine were added simultaneously to toluene and refluxed for 24 h. We were pleased to find that the corresponding PCP pincer complexes 4 could be obtained in 46% isolated yields upon workup. It should be pointed out that the yields of PCN complexes 2 and 3 decreased obviously if PdCl₂ was added with chlorophosphine and other reactants at the same time. In the previously reported synthetic

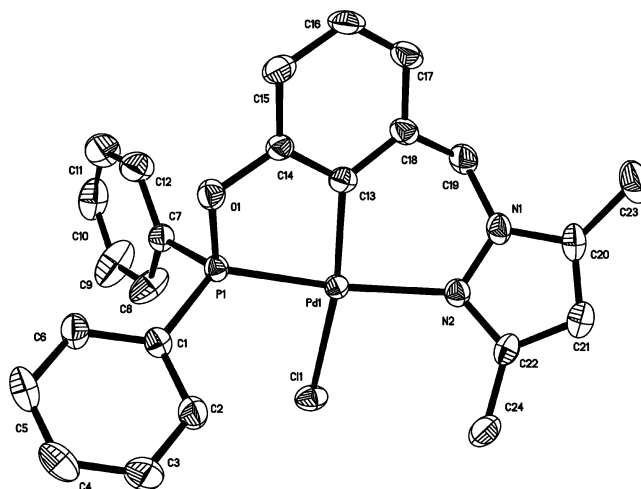


Figure 1. Molecular structure of 2a. Hydrogen atoms are omitted for clarity.

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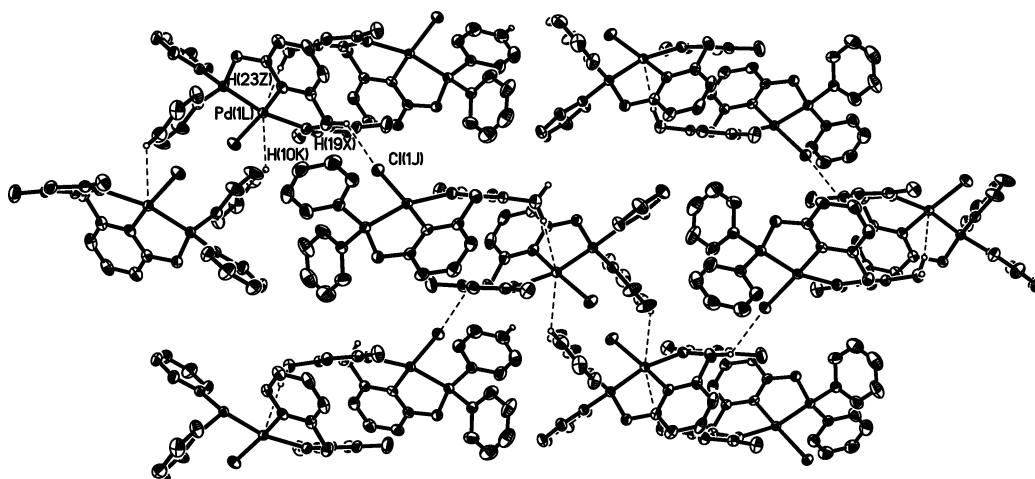


Figure 2. 2D layer structure of complex **2a** formed by hydrogen bonds. Non-hydrogen-bonding H atoms are omitted for clarity.

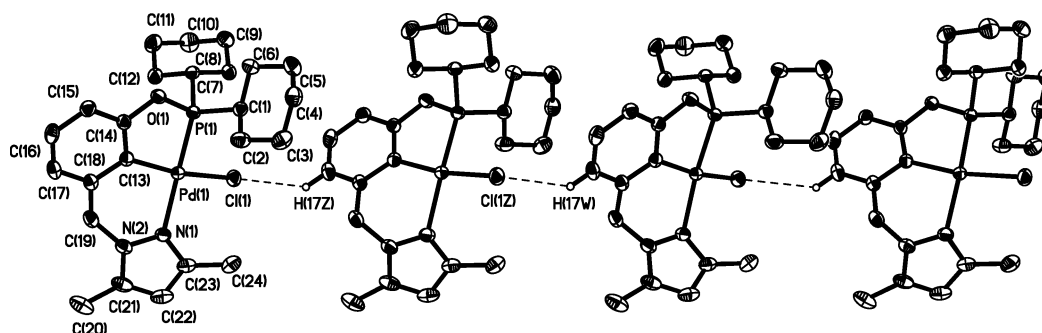


Figure 3. One-dimensional chain structure of complex **2b** formed by C–H···Cl hydrogen bonds. Non-hydrogen-bonding H atoms are omitted for clarity.

methods for the preparation of pincer palladium complexes with mono- or diphosphinite ligands, the air- and moisture-sensitive ligands needed to be constructed and isolated before the metalation reaction, except for the ligand introduction method described by Uozumi et al. Therefore, the current one-pot phosphorylation/palladation strategy has the evident advantages of avoiding this troublesome isolation step and thus simplifying the synthetic procedure. At the same time, the direct C2 palladation via C–H activation of the related ligands was successfully accomplished during the reaction by using cheap and commercially available palladium chloride (about 10\$/g). As for the preparation of PCP–bis(phosphinite) pincer complexes, we noticed that only one account had been reported concerning one-pot phosphorylation/palladation reaction, and $\text{PdCl}_2(\text{COD})$, which could be synthesized from PdCl_2 ,⁷ was added after the phosphorylation reaction.^{3k} Uozumi's synthetic route^{3j} required one to prepare 2-iodoresorcinol (72% yield) from resorcinol.⁸

All of the pincer complexes are air- and moisture-stable both in the solid state and in solution. They were fully characterized by elemental analysis, ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR, DEPT, HSQC, IR, and ESI-MS.

Molecular Structures of Complexes 2a–d. The molecular structures of PCN pincer palladium complexes **2a–d** were determined by X-ray single crystal analysis. The molecules are shown in Figures 1–6 (displacement ellipsoids are drawn at the 30% probability level). Selected bond lengths and bond angles are listed in Table 1. The palladium atom in each complex

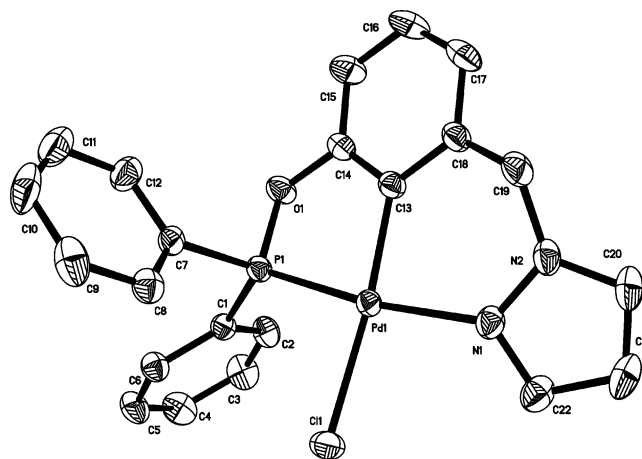


Figure 4. Molecular structure of **2c**. Hydrogen atoms are omitted for clarity.

adopts a typical distorted-square-planar configuration defined by the phosphinito P atom, the carbon atom of central aryl ring, the pyrazolyl N atom, and the chlorine atom. In the two formed palladacycles, one is five-membered and the other is a six-membered metallacycle. It is found that the former shows an envelope conformation and the latter reveals a boat conformation. All of the bond lengths and angles around Pd(II) in **2a–d** are similar except a smaller N–Pd–P angle (161.2°) in **2b**. The Pd–C bond lengths are around 2.01 Å, which are comparable to those found in the PCP–bis(phosphinite) pincer palladium complexes (1.97–2.02 Å).^{3a,b,j} The Pd–P bond lengths (2.18–2.20 Å) are slightly shorter than those of bis(phosphinite) complexes (2.26–2.29 Å).^{3a,b,j} The C–Pd–Cl angles are in the range 168.6 – 174.7° , and the N–Pd–P angles of **2a**, **2c**, and

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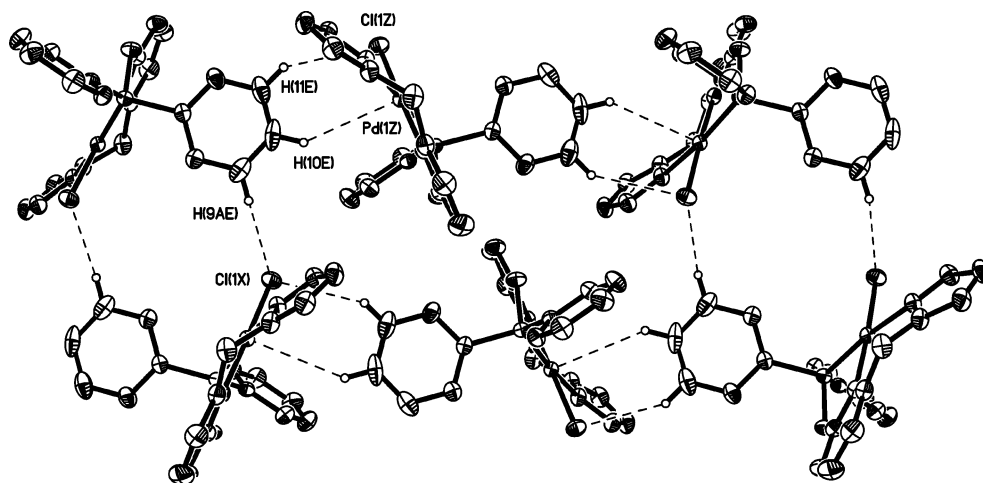


Figure 5. 2D layer structure of complex **2c** formed by hydrogen bonds. Non-hydrogen-bonding H atoms are omitted for clarity.

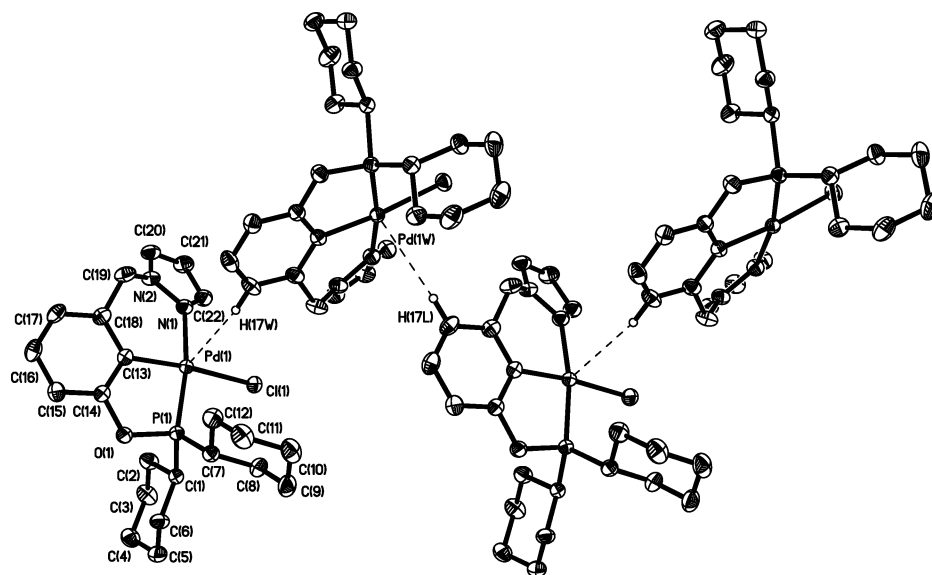


Figure 6. One-dimensional zigzag chain structure of complex **2d** formed by C–H...Pd hydrogen bonds. Non-hydrogen-bonding H atoms are omitted for clarity.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for PCN Complexes **2a–d**

	compound			
	2a	2b	2c	2d
Pd(1)–C(13)	2.009(4)	2.005(3)	2.009(3)	2.012(3)
Pd(1)–N(1)		2.139(3)	2.098(3)	2.111(2)
Pd(1)–N(2)	2.159(4)			
Pd(1)–P(1)	2.1937(12)	2.1860(12)	2.1823(8)	2.1966(8)
Pd(1)–Cl(1)	2.3931(12)	2.3996(10)	2.3829(9)	2.3959(10)
C(13)–Pd(1)–N(1)		90.86(13)	91.82(12)	92.36(11)
C(13)–Pd(1)–N(2)	90.54(17)			
C(13)–Pd(1)–P(1)	79.59(14)	80.55(10)	80.24(9)	81.70(9)
N(1)–Pd(1)–P(1)		161.20(8)	171.56(8)	169.82(7)
N(2)–Pd(1)–P(1)	166.62(10)			
C(13)–Pd(1)–Cl(1)	169.71(12)	168.63(9)	174.33(9)	174.69(9)
N(1)–Pd(1)–Cl(1)		97.74(9)	93.85(8)	91.88(8)
N(2)–Pd(1)–Cl(1)	97.58(11)			
P(1)–Pd(1)–Cl(1)	93.30(5)	93.25(4)	94.09(4)	93.63(3)

2d are 166.6–171.6°. In comparison with the P–Pd–P angles (around 160°) in the PCP–bis(phosphinite) complexes, which have two equivalent five-membered palladacycles,^{3a,b,j} the bigger N–Pd–P angles in the present PCN complexes suggest that introduction of a larger metallacycle decreases the steric strain of the resultant complexes.

In complex **2a**, chlorine atom forms a CH...Cl hydrogen bond with the adjacent –CH₂– group (Cl1J...H19X = 2.890 Å).⁹ In addition, Pd atom not only forms a hydrogen bond with the adjacent C–H group of the benzene ring (Pd1L...H10K = 2.805 Å), but also forms a hydrogen bond with the adjacent –CH₃ group (Pd1L...H23Z = 2.981 Å),¹⁰ which are attributed to construct the 2D layer structure of **2a** (Figure 2). Complex **2c** also has a 2D layer structure formed by two types of C–H...X hydrogen bonds and a type of CH...M hydrogen bond, which stabilize the conformation with 2.881 Å for Cl1X...H9AE, 2.886 Å for Cl1Z...H11E, and 3.124 Å for Pd1Z...H10E (Figure 5). In the crystal of **2b**, there exist CH...Cl hydrogen bonds between chlorine atom and the adjacent C–H group of benzene ring (Cl1...H17Z = Cl1Z...H17W = 2.884 Å), giving the one-dimensional chain structure of complex **2b** (Figure 3). Complex **2d** like **2b** also has a one-dimensional chain structure (Figure 6). However, the chlorine atom does not participate in hydrogen

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bonding and the Pd atom forms a CH $\cdots$ M hydrogen bond (Pd1 $\cdots$ H17W = Pd1W $\cdots$ H17L = 3.200 Å) instead.

The catalytic activities of all of the obtained PCN and PCP complexes toward Suzuki reactions of aryl halides with phenylboronic acid were tested and compared (see Supporting Information).

Conclusions

We have developed a facile, direct method based on the one-pot phosphorylation/palladation reaction for the preparation of PCN and PCP pincer palladium complexes containing phosphinito group(s). A wide variety of such complexes can be readily constructed from various chlorophosphines and/or N-donors. We are currently extending this one-pot synthetic strategy to include chiral PCN pincer palladium complexes and also further investigating the applications of the obtained complexes in Pd-catalyzed reactions. The results will be reported in due course.

Experimental Section

General Procedures. All reactions were carried out under nitrogen atmosphere. Solvents were dried with standard methods and freshly distilled prior to use except that in the Suzuki reactions the solvents were analytical grade and used without further purification. 3-Hydroxybenzylbromide¹¹ and 3,5-dimethylpyrazole¹² were prepared according to the published procedures. All other chemicals were used as purchased. Melting points were measured on a WC-1 microscopic apparatus and were uncorrected. Elemental analyses were determined with a Thermo Flash EA 1112 elemental analyzer. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ¹H, ¹³C{¹H} NMR, and ³¹P{¹H} NMR spectra were recorded on a Bruker DPX-400 spectrometer in CDCl₃ with TMS as an internal standard for ¹H, ¹³C{¹H} NMR and 85% H₃PO₄ as the external standard for ³¹P{¹H} NMR. Mass spectra were performed on the Agilent LC/MSD Trap XCT instrument.

Synthesis of Pyrazolyl or Amino-Containing *m*-Phenol Derivatives. Under nitrogen atmosphere, a mixture of 3-hydroxybenzylbromide (374 mg, 2 mmol), 3,5-dimethylpyrazole or pyrazole (2 mmol), and NaH (144 mg, 6 mmol) in 30 mL of dioxane was refluxed with stirring for 3 days. After being cooled, the reaction was quenched with water, and the pH value of the solution was adjusted to about 6. The aqueous layer was then extracted with dichloromethane, and the organic layers were dried over MgSO₄, filtered, and evaporated. The crude was purified by recrystallization from acetone for **1a** or by preparative TLC on silica gel plates eluting with CH₂Cl₂/acetone (2:1) for **1b**. 1-(Diethylaminomethyl)-3-hydroxybenzene was prepared by a similar procedure. K₂CO₃ instead of NaH was used, and the reaction mixture was refluxed for 5 h. After being cooled, the reaction was quenched with water, and the pH value of the solution was adjusted to about 6. Saturated NaHCO₃ solution was then added, and the aqueous layer was extracted with ethyl acetate. The organic layers were dried over MgSO₄, filtered, and evaporated. The residue was purified by preparative TLC on silica gel plates eluting with ethyl acetate. ¹H NMR (400 MHz, CDCl₃): δ 7.10–7.08 (m, 1H, Ar–H), 6.81 (s, 1H, Ar–H), 6.78 (d, *J* = 7.5 Hz, 1H, Ar–H), 6.70 (d, *J* = 7.9 Hz, 1H, Ar–H), 3.55 (s, 2H, CH₂), 2.57 (q, *J* = 7.1 Hz, 4H, CH₂CH₃), 1.05 (t, *J* = 7.1 Hz, 6H, CH₂CH₃).

1-(3,5-Dimethylpyrazol-1-ylmethyl)-3-hydroxybenzene (1a). 316 mg, 78% yield, white solids. mp 150–152 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.09 (t, *J* = 7.8 Hz, 1H, Ar–H), 6.66 (dd, *J* =

1.9, 8.0 Hz, 1H, Ar–H), 6.61 (d, *J* = 7.5 Hz, 1H, Ar–H), 6.27 (s, 1H, Ar–H), 5.85 (s, 1H, =CH), 5.13 (s, 2H, CH₂), 2.09 (s, 3H, CH₃), 2.02 (s, 3H, CH₃). IR (KBr, cm^{−1}): 1602, 1554, 1459, 1382, 1267, 1155, 1128, 1038, 866, 781, 742, 711. Anal. Calcd for C₁₂H₁₄N₂O: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.31; H, 7.16; N, 13.72.

1-(Pyrazol-1-ylmethyl)-3-hydroxybenzene (1b). 256 mg, 74% yield, pale yellow solids. mp 50–70 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, *J* = 1.7 Hz, 1H, =CH), 7.39 (d, *J* = 2.2 Hz, 1H, =CH), 7.09 (t, *J* = 7.9 Hz, 1H, Ar–H), 6.69 (dd, *J* = 2.0, 8.1 Hz, 1H, Ar–H), 6.63 (d, *J* = 7.6 Hz, 1H, Ar–H), 6.45 (s, 1H, Ar–H), 6.28 (t, *J* = 2.0 Hz, 1H, =CH), 5.20 (s, 2H, CH₂). IR (KBr, cm^{−1}): 1618, 1588, 1490, 1381, 1291, 1249, 1219, 1149, 1088, 1055, 977, 934, 881, 765, 689. Anal. Calcd for C₁₀H₁₀N₂O: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.98; H, 5.84; N, 15.84.

General Procedure for the Synthesis of PCN Pincer Palladium Complexes. To a stirred solution of **1a**, **1b**, or 1-(diethylaminomethyl)-3-hydroxybenzene (1 mmol) and triethylamine (168 μL, 1.2 mmol) in toluene (20 mL) was added diphenylchlorophosphine or dicyclohexylchlorophosphine (1.2 mmol) under N₂ atmosphere at rt. The resultant mixture was refluxed for 6 h. PdCl₂ (177 mg, 1 mmol) was then added, and the reaction mixture was refluxed for another 18 h. After cooling, filtration, and evaporation, the residue was purified by preparative TLC on silica gel plates eluting with CH₂Cl₂/petroleum ether (3:1) to afford the corresponding PCN pincer complexes.

2-(3,5-Dimethylpyrazol-1-ylmethyl)-6-(diphenylphosphinoxy)-phenylchloropalladium(II) (2a). 329 mg, 62% yield, white solids. mp 256–258 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.06–8.01 (m, 4H, Ph–H), 7.55–7.46 (m, 6H, Ph–H), 7.03 (dt, *J* = 1.6, 7.9 Hz, 1H, Ar–H), 6.92 (d, *J* = 7.9 Hz, 1H, Ar–H), 6.79 (d, *J* = 7.3 Hz, 1H, Ar–H), 5.89 (s, 1H, =CH), 5.04 (s, 2H, CH₂), 2.66 (s, 3H, CH₃), 2.36 (s, 3H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 163.7, 152.1, 139.9, 138.7, 138.3, 132.9, 132.4, 132.3, 132.1, 128.7, 128.6, 127.0, 120.9, 112.0, 107.2, 53.2, 15.3, 11.8. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 154.4. IR (KBr, cm^{−1}): ν 1551, 1469, 1428, 1382, 1356, 1286, 1222, 1107, 1031, 991, 836, 781, 742, 710. Anal. Calcd for C₂₄H₂₂ClN₂OPPd: C, 54.67; H, 4.21; N, 5.31. Found: C, 54.37; H, 4.22; N, 5.05. MS-ESI⁺: *m/z* 491.1 ([M – Cl]⁺).

2-(3,5-Dimethylpyrazol-1-ylmethyl)-6-(dicyclohexylphosphinoxy)phenylchloropalladium(II) (2b). 364 mg, 68% yield, white solids. mp > 260 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.96 (dt, *J* = 1.3, 7.7 Hz, 1H, Ar–H), 6.74 (d, *J* = 7.9 Hz, 1H, Ar–H), 6.73 (d, *J* = 7.2 Hz, 1H, Ar–H), 5.85 (s, 1H, =CH), 5.00 (s, 2H, CH₂), 2.65 (s, 3H, CH₃), 2.34 (s, 3H, CH₃), 2.36–2.33 (m, 2H, Cy), 2.24–2.22 (m, 2H, Cy), 1.86–1.61 (m, 12H, Cy), 1.40–1.24 (m, 6H, Cy). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 165.3, 151.7, 139.6, 138.7, 137.4, 126.4, 120.3, 110.8, 107.0, 53.3, 38.1, 37.8, 27.2, 26.9, 26.5, 26.4, 26.3, 25.8, 15.1, 11.7. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 195.7. IR (KBr, cm^{−1}): ν 2929, 2851, 1548, 1445, 1421, 1293, 1223, 1036, 888, 835, 784, 760. Anal. Calcd for C₂₄H₃₄ClN₂OPPd: C, 53.44; H, 6.35; N, 5.19. Found: C, 53.74; H, 6.48; N, 4.86. MS-ESI⁺: *m/z* 503.3 ([M – Cl]⁺).

2-(Pyrazol-1-ylmethyl)-6-(diphenylphosphinoxy)phenylchloropalladium(II) (2c). 356 mg, 72% yield, white solids. mp > 260 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.43 (d, *J* = 2.0 Hz, 1H, =CH), 8.03–7.98 (m, 4H, Ph–H), 7.64 (d, *J* = 2.0 Hz, 1H, =CH), 7.53–7.44 (m, 6H, Ph–H), 7.07 (dt, *J* = 1.7, 7.9 Hz, 1H, Ar–H), 6.98 (d, *J* = 7.5 Hz, 1H, Ar–H), 6.80 (d, *J* = 7.1 Hz, 1H, Ar–H), 6.36 (s, 1H, =CH), 5.22 (s, 2H, CH₂). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 164.4, 142.9, 137.2, 136.6, 132.8, 132.2, 132.1, 132.0, 128.8, 128.6, 127.1, 121.1, 112.2, 106.1, 57.3. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 156.8. IR (KBr, cm^{−1}): ν 2927, 1426, 1371, 1276, 1211, 1163, 1109, 1067, 1028, 984, 940, 848, 778, 747, 704. Anal. Calcd for C₂₂H₁₈ClN₂OPPd: C, 52.93; H, 3.63; N, 5.61. Found: C, 53.14; H, 3.66; N, 5.43. MS-ESI⁺: *m/z* 463.6 ([M – Cl]⁺), 523.3 ([M + Na]⁺), 963.2 ([2M – Cl]⁺).

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Table 2. Summary of Crystal Structure Determination for PCN Complexes 2a–d

	2a	2b	2c	2d
formula	C ₂₄ H ₂₂ ClN ₂ OPPd	C ₂₄ H ₃₄ ClN ₂ OPPd	C ₂₂ H ₁₈ ClN ₂ OPPd	C ₂₂ H ₃₀ ClN ₂ OPPd
<i>M</i> _r	527.26	539.35	499.20	511.30
cryst size [mm]	0.20 × 0.18 × 0.16	0.20 × 0.18 × 0.17	0.20 × 0.18 × 0.16	0.20 × 0.16 × 0.16
<i>a</i> [Å]	17.515(4)	18.559(4)	9.798(2)	9.7206(19)
<i>b</i> [Å]	14.425(3)	8.2434(16)	17.997(4)	23.522(5)
<i>c</i> [Å]	18.312(4)	17.756(4)	11.691(2)	10.375(2)
α [deg]	90	90	90	90
β [deg]	103.20(3)	114.69(3)	100.46(3)	109.16(3)
γ [deg]	90	90	90	90
<i>V</i> [Å ³]	4504.4(16)	2468.2(8)	2027.3(7)	2240.9(8)
<i>Z</i>	8	4	4	4
space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>
<i>D</i> _{calcd} [g cm ^{−3}]	1.555	1.451	1.636	1.516
<i>μ</i> [mm ^{−1}]	1.032	0.943	1.141	1.034
θ range [deg]	1.19–25.50	1.21–25.49	2.10–25.50	1.73–25.50
no. of data collected	13990	7744	6556	7353
no. of unique data	8056	4360	3673	3978
obsd data [<i>I</i> ≥ 2σ(<i>I</i>)]	6909	3725	3366	3655
<i>R</i> (all data)	0.0621	0.0451	0.0365	0.0369
<i>R</i> _w (all data)	0.1307	0.0851	0.0735	0.0868
<i>F</i> (000)	2128	1112	1000	1048
peak/hole [e Å ^{−3}]	0.951/−0.933	0.329/−0.483	0.347/−0.492	0.348/−0.678

2-(Pyrazol-1-ylmethyl)-6-(dicyclohexylphosphinoxy)phenylchloropalladium (II) (2d). 300 mg, 59% yield, white solids. mp > 260 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.43 (s, 1H, =CH), 7.66 (s, 1H, =CH), 7.06 (t, *J* = 7.6 Hz, 1H, Ar–H), 6.84 (d, *J* = 7.9 Hz, 1H, Ar–H), 6.80 (d, *J* = 7.3 Hz, 1H, Ar–H), 6.40 (s, 1H, =CH), 5.25 (s, 2H, CH₂), 2.38–2.32 (m, 2H, Cy), 2.25–2.22 (m, 2H, Cy), 1.87–1.62 (m, 12H, Cy), 1.41–1.24 (m, 6H, Cy). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 165.7, 142.1, 137.0, 135.6, 131.7, 126.4, 120.4, 110.9, 105.7, 57.3, 37.5, 37.3, 26.8, 26.6, 26.2, 26.1, 26.0, 25.5. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 196.7. IR (KBr, cm^{−1}): ν 2930, 2852, 1633, 1555, 1445, 1420, 1380, 1281, 1228, 1173, 1116, 1071, 995, 944, 845, 766. Anal. Calcd for C₂₂H₃₀ClN₂OPPd: C, 51.68; H, 5.91; N, 5.48. Found: C, 51.92; H, 5.99; N, 5.10. MS-ESI⁺: *m/z* 475.7 ([M – Cl]⁺), 535.4 ([M + Na]⁺), 987.4 ([2M – Cl]⁺).

2-(Diethylaminomethyl)-6-(diphenylphosphinoxy)phenylchloropalladium(II) (3). 272 mg, 54% yield, white solids. mp 216–217 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.03–7.97 (m, 4H, Ph–H), 7.48–7.46 (m, 6H, Ph–H), 7.00 (t, *J* = 7.8 Hz, 1H, Ar–H), 6.76 (d, *J* = 7.9 Hz, 1H, Ar–H), 6.71 (d, *J* = 7.5 Hz, 1H, Ar–H), 4.18 (s, 2H, CH₂), 3.46–3.41 (m, 2H, CH₂CH₃), 2.89–2.82 (m, 2H, CH₂CH₃), 1.48 (t, *J* = 7.1 Hz, 6H, CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 162.7, 152.0, 145.6, 134.7, 134.1, 132.6, 132.4, 132.3, 129.6, 129.5, 127.4, 116.8, 110.2, 66.4, 56.3, 14.3. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 152.4. IR (KBr, cm^{−1}): ν 3050, 2966, 2925, 2859, 1460, 1430, 1226, 1107, 995, 830, 772, 749, 703. Anal. Calcd for C₂₃H₂₅ClN₂OPPd: C, 54.78; H, 5.00; N, 2.78. Found: C, 54.92; H, 5.14; N, 2.56. MS-ESI⁺: *m/z* 468.3 ([M – Cl]⁺), 528.2 ([M + Na]⁺), 973.1 ([2M – Cl]⁺).

General Procedure for the Synthesis of PCP Pincer Palladium Complexes. To a stirred solution of resorcinol (55 mg, 0.5 mmol), PdCl₂ (90 mg, 0.5 mmol), and triethylamine (280 μL, 2.0 mmol) in toluene (20 mL) was added diphenylchlorophosphine or dicyclohexylchlorophosphine (1.2 mmol) under N₂ atmosphere at rt. The resultant mixture was refluxed for 24 h. After cooling, filtration, and evaporation, the residue was purified by preparative TLC on silica gel plates eluting with CH₂Cl₂ to afford the corresponding PCP pincer complexes.

2,6-Bis(diphenylphosphinoxy)phenylchloropalladium(II) (4a).^{3e} 141 mg, 46% yield, white solids. ¹H NMR (400 MHz, CDCl₃): δ 8.00–7.95 (m, 8H, Ph–H), 7.52–7.47 (m, 12H, Ph–H), 7.09 (t, *J* = 8.0 Hz, 1H, Ar–H), 6.75 (d, *J* = 8.0 Hz, 2H, Ar–H).

2,6-Bis(dicyclohexylphosphinoxy)phenylchloropalladium(II) (4b). 149 mg, 46% yield, white solids. mp 199–202 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.95 (t, *J* = 8.0 Hz, 1H, Ar–H), 6.51 (d, *J* = 8.0 Hz, 2H, Ar–H), 2.29–2.23 (m, 4H, Cy), 2.04–2.00 (m, 4H, Cy), 1.93–1.82 (m, 12H, Cy), 1.71–1.53 (m, 12H, Cy), 1.39–1.22 (m, 12H, Cy). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 166.3, 129.6, 127.9, 105.8, 37.9, 37.8, 37.7, 27.0, 26.7, 26.5, 26.4, 26.3, 25.8. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 181.7. IR (KBr, cm^{−1}): 2928, 2850, 1567, 1442, 1243, 1221, 1179, 1112, 1001, 888, 849, 761. Anal. Calcd for C₃₀H₄₇ClO₂P₂Pd: C, 55.99; H, 7.36. Found: C, 55.98; H, 7.18. MS-ESI⁺: *m/z* 608.0 ([M – Cl]⁺), 1251.5 ([2M – Cl]⁺).

X-ray Diffraction Studies. Crystals of PCN pincer complexes 2a–d were obtained by recrystallization from dichloromethane and petroleum ether at ambient temperature. All diffraction data were collected with a Rigaku-IV imaging plate area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The diffraction data were corrected for Lorentz and polarization factors. The structures were solved by direct methods¹³ and expanded using Fourier techniques and refined by full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. Their raw data were corrected, and the structures were solved using the SHELXL-97 program.¹⁴ Details of crystal structure determination of complexes 2a–d are summarized in Table 2.

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Supporting Information Available: Applications of complexes 2–4 to the Suzuki reactions and their ¹H NMR, ¹³C{¹H} NMR, ³¹P{¹H} NMR, as well as ESI-MS spectra. Full crystallographic data for compounds 2a–d are available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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