PCP Pincer Palladium Complexes and Their Catalytic Properties: Synthesis via the Electrophilic Ligand Introduction Route

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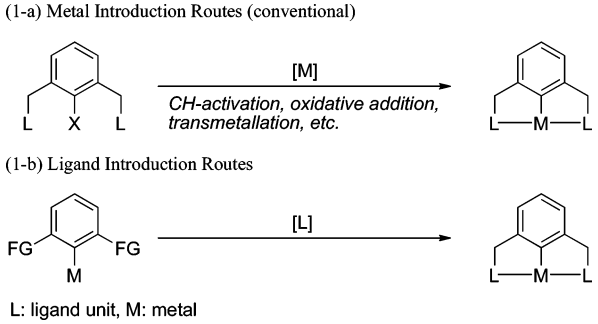
A variety of PCP pincer palladium complexes having phosphinito groups [2,6-$(R_2PO)_2C_6H_3PdI$ (R = alkyl, aryl and Et_2N)] were synthesized via the electrophilic ligand introduction route with high efficiency. Thus, *trans*-(2,6-dihydroxyphenyl)iodobis(triphenylphosphine)palladium was prepared by the reaction of 2-iodoresorcinol with tetrakis(triphenylphosphine)palladium, and the palladium complex was converted to the PCP pincer palladium complexes by treatment with chlorophosphines in the presence of triethylamine in 82−95% yield. X-ray molecular structure analyses of the pincer complexes revealed that the molecules adopted distorted square-planar geometries. The Suzuki coupling reaction of 4-bromoacetophenone with phenylboronic acid took place in the presence of 0.1−0.01 mol % of the pincer complexes to give 4-acetylbiphenyl with turnover numbers of 328−5790.

Introduction

Pincer complexes containing terdentate monoanionic ligands composed of an anionic aryl carbon atom and two mutually *trans*-chelating donor sites at the 2,6-positions of the aromatic ring have attracted much attention not only as highly active catalysts in synthetic organic chemistry[1] but also as organometallic materials in the field of materials science.[2] Consequently, considerable effort has been devoted toward the development of synthetic methods for pincer complexes over the past decade.[1d,2] Conventional methods use metal introduction routes, in which the ligand frameworks are initially constructed, followed by metalation of the ligands to give the pincer complexes (Scheme 1 (1-a)).[3]

However, these methods are not suitable for the synthesis of pincer complexes having bulky and/or chemically unstable ligand units. Recently, we developed a new synthetic strategy, *the ligand introduction route*, in which the metal is introduced to the aromatic ring prior to the construction of the ligand units (Scheme 1 (1-b)). With this synthetic strategy, a novel class of NCN pincer palladium complexes **1** and **2**, having bulky pyrroloimidazolone groups and moisture-sensitive imino groups, respectively, which were difficult to synthesize via conventional metal introduction routes, was successfully synthesized with high efficiency.[4] In these cases, nucleophilic proline anilides and primary amines reacted with the electrophilic formyl groups at the 2,6-positions of the metalated aromatic ring (Scheme 2 (2-a)).

Scheme 1. Synthetic Strategies for Pincer Complexes



The electrophilic ligand introduction route, in which the coordinative electrophiles are introduced to the nucleophilic functional groups at the 2,6-positions of the aromatic ring, is an alternative method for the synthesis of the pincer complexes (Scheme 2 (2-b)). If this concept was applied to the synthesis of pincer complexes via an electrophilic ligand introduction route, a wide variety of pincer complexes could be obtained by the combination of the coordinative electrophiles and the nucleophilic functional groups. We report here the synthesis of PCP pincer palladium complexes having phosphinito groups via the electrophilic ligand introduction route, their structures, and their catalytic activities in the Suzuki coupling reaction.

Results and Discussion

Synthesis of PCP Pincer Palladium Complexes. As a key precursor, we designed *trans*-(2,6-dihydroxyphenyl)iodobis(triphenylphosphine)palladium, **4**, in which two nucleophilic hydroxy groups were attached to the 2,6-positions of the benzene ring (Scheme 2). The electrophilic introduction of the R_2P− groups to the hydroxy groups of the palladium complex **4** would lead to the formation of the PCP pincer palladium complexes having the phosphinito groups **5** along with the dissociation of triphenylphosphine. The palladium complex **4** was readily prepared by the oxidative addition of 2-iodoresorcinol (**3**) to

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(1) Reviews: (a) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (b) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837. (c) Bedford, R. B. *Chem. Commun.* **2003**, 1787. (d) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527. (e) Szabó, K. J. *Synlett* **2006**, 811.

(2) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

(3) For the preparation of PCP pincer complexes having phosphinoxy groups via metal introduction routes, see: (a) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379. (b) Bedford, R. B.; Draper, S. M.; Scully, P. N.; Welch, S. L. *New J. Chem.* **2000**, *24*, 745. (c) Morales-Morales, D.; Grause, C.; Kasaoka, K.; Redón, R.; Cramer, R. E.; Jensen, C. M. *Inorg. Chim. Acta* **2000**, *300*−*302*, 958. (d) Wallner, O. A.; Szabó, K. J. *Org. Lett.* **2004**, *6*, 1829. (e) Wallner, O. A.; Olsson, V. J.; Eriksson, L.; Szabó, K. J. *Inorg. Chim. Acta* **2006**, *359*, 1767.

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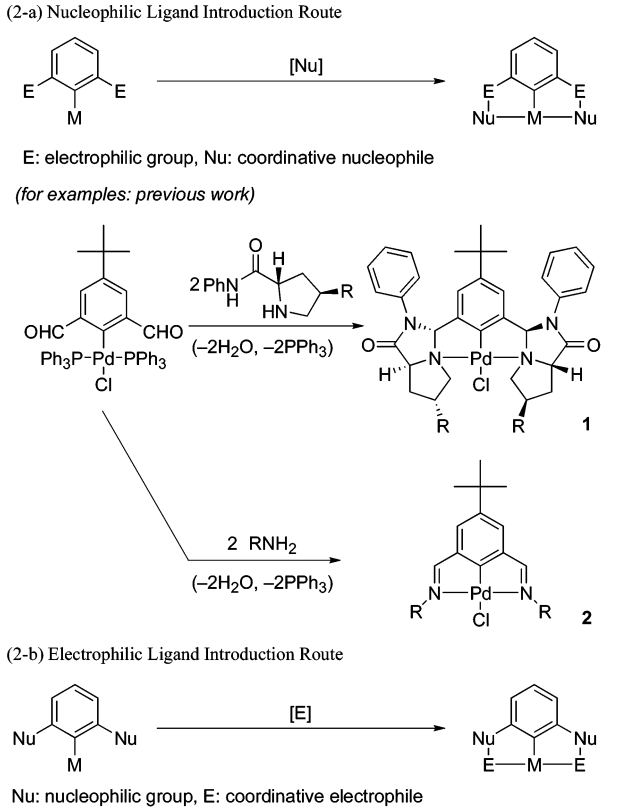
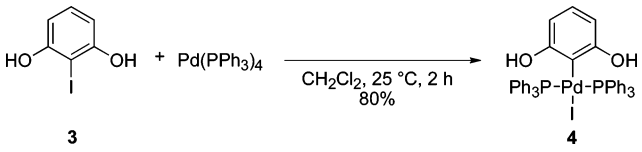
Scheme 2. Synthetic Strategies for Pincer Complexes via Ligand Introduction Routes



Scheme 3. Synthesis of Palladium Complex 4



tetrakis (triphenylphosphine) palladium in 80% yield (Scheme 3). The structure of the palladium complex **4** was unequivocally determined by X-ray molecular structure analysis (Figure 1).

The palladium complex **4** adopts a square-planar structure in which two phosphorus atoms of triphenylphosphines, the iodine atom, and the carbon atom of the benzene ring are attached to the central palladium atom, and two phosphorus atoms are located *trans* to each other. The dihydroxyphenyl group is oriented almost perpendicularly with respect to the square plane.

With the key precursor **4** in hand, we examined the synthesis of PCP pincer palladium complexes **5** (Table 1). As expected, the palladium complex **4** reacted with 2.2 equiv of chlorodiphenylphosphine in the presence of triethylamine in toluene at 25 °C for 1 h to give the PCP pincer palladium complex having diphenylphosphinito groups **5a** in 92% yield (entry 1). Similarly, the pincer complex having the bis(*o*-tolyl)phosphinito groups **5b** was obtained in 92% yield (entry 2). Encouraged by these results, we turned our attention to the synthesis of the pincer complexes having dialkylphosphinito groups. In general, trivalent organophosphorus compounds having *P*-alkyl groups are

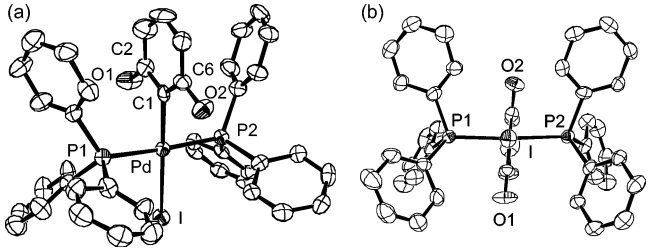


Figure 1. (a) ORTEP drawing of the palladium complex **4**·CH_2Cl_2 with a thermal ellipsoid plot (50% probability). (b) ORTEP drawing of **4**·CH_2Cl_2 along the I−Pd bond. Hydrogen atoms and solvated CH_2Cl_2 are omitted for clarity. Selected bond lengths (Å) and angles (deg): I−Pd = 2.7014(8), Pd−P1 = 2.343(3), Pd−P2 = 2.322(3), Pd−C1 = 2.051(9), P1−Pd−P2 = 173.42(9), P1−Pd−C1 = 87.4(3), P1−Pd−I = 93.99(6), P2−Pd−C1 = 87.4(3), P2−Pd−I = 91.48(6), C1−Pd−I = 176.8(2), P1−Pd−C1−C2 = −86.6(8), P2−Pd−C1−C6 = −83.9(8).

Table 1. Synthesis of Pincer Complexes 5 via Electrophilic Ligand Introduction Route[a]

4 + R_2PCl → (Et_3N, toluene, 25 °C, time) → **5**

entry	R	5	time (h)	yield (%)
1	C_6H_5	**5a**	1	92
2	2-$CH_3C_6H_4$	**5b**	24	92
3	CH_3CH_2	**5c**	0.5	86
4	$(CH_3)_2CH$	**5d**	1	95
5	cyclo-C_6H_{11}	**5e**	3	82
6	$(CH_3CH_2)_2N$	**5f**	1	94

[a] The reaction was carried out with the palladium complex **4** (0.25 mmol), chlorophosphine (0.55 mmol), and triethylamine (0.55 mmol) in toluene (2.5 mL) at 25 °C.

readily oxidized in air; therefore, the synthesis of PCP pincer complexes having dialkylphosphinito groups via the conventional metal introduction routes is laborious. Nevertheless, the pincer complexes having diethyl- **5c**, diisopropyl- **5d**, and dicyclohexylphosphinito groups **5e** were readily synthesized by the reaction of the palladium complex **4** with the corresponding dialkylchlorophosphines in 86%, 95%, and 82% yield, respectively (entries 3−5). The reaction of the palladium complex **4** with bis(diethylamino)chlorophosphine gave the pincer complex having the bis(diethylamino)phosphinito groups **5f** in 94% yield (entry 6). The resulting pincer complexes **5** are stable in air and can be purified by column chromatography on silica gel.

Molecular Structures of PCP Pincer Palladium Complexes. The structures of the pincer complexes **5a**−**f** were unambiguously determined by X-ray molecular structure analyses (Figure 2, Table 2).[3a−c,5] In all cases, the pincer complexes **5** adopt distorted square-planer geometries at the palladium atom with two phosphorus atoms of the phosphinito groups, the iodine atom, and the carbon atom of the benzene ring. The palladium−carbon bond lengths of the pincer complexes **5** (1.98−2.02 Å) are slightly shorter than that of the palladium complex **4** (2.05 Å) by 0.03−0.07 Å because of the intramolecular coordination of the phosphinito ligands. The I−Pd−C1 angles of the pincer complexes **5** (175.0−179.3°) are almost linear, whereas the P1−Pd−P2 angles (159.9−160.8°) are bent due to the constraints imposed by the atoms forming the two fused five-membered rings.

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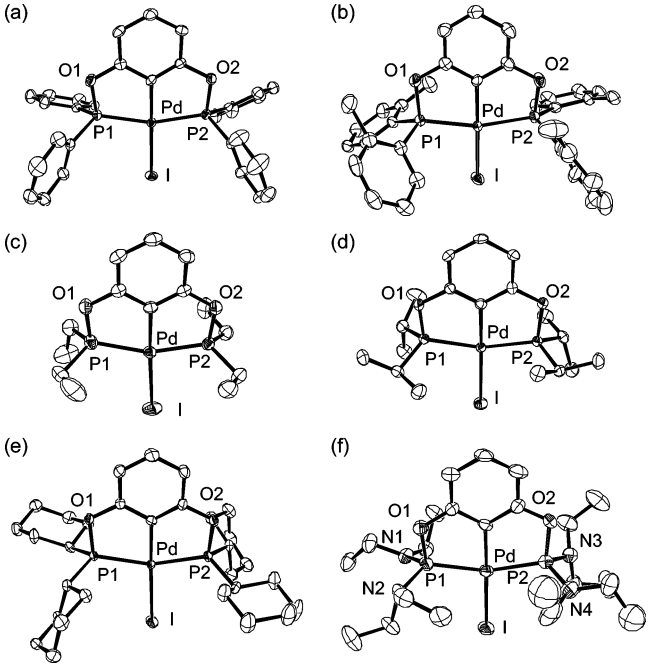


Figure 2. ORTEP drawings of PCP pincer palladium complexes **5** with a thermal ellipsoid plot (50% probability): (a) 2,6-$[(C_6H_5)_2PO]_2C_6H_3PdI$, **5a**, (b) 2,6-$[(2\text{-}CH_3C_6H_4)_2PO]_2C_6H_3PdI$, **5b**, (c) 2,6-$[(CH_3CH_2)_2PO]_2C_6H_3PdI$, **5c**, (d) 2,6-$\{[(CH_3)_2CH]_2PO\}_2C_6H_3PdI$, **5d**, (e) 2,6-$[(c\text{-}C_6H_{11})_2PO]_2C_6H_3PdI$, **5e**, and (f) 2,6-$\{[(CH_3CH_2)_2N]_2PO\}_2C_6H_3PdI$, **5f**. Hydrogen atoms are omitted for clarity. Two independent molecules were present in one asymmetric unit of **5c** and **5d**. One is shown.

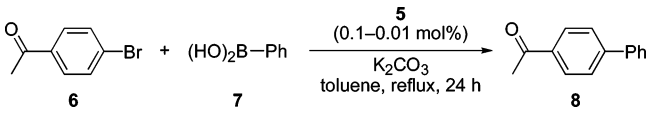
Table 2. Selected Bond Lengths (Å) and Angles (deg) for PCP Pincer Palladium Complexes 5

	bond lengths (Å)				angles (deg)	
5	Pd−I	Pd−P1	Pd−P2	Pd−C1	P1−Pd−P2	I−Pd−C1
5a	2.6402(2)	2.2642(7)	2.2672(8)	1.992(3)	160.30(2)	179.34(7)
5b	2.6515(7)	2.294(2)	2.279(2)	2.021(7)	159.90(7)	175.0(2)
5c	2.6450(4)	2.279(1)	2.2609(9)	1.988(3)	160.20(3)	176.05(9)
5d	2.6605(3)	2.2778(8)	2.2733(8)	1.999(3)	160.02(3)	176.56(8)
5e	2.6408(4)	2.286(1)	2.273(1)	1.981(4)	160.77(4)	175.7(1)
5f	2.6624(6)	2.284(2)	2.277(2)	1.990(6)	160.84(6)	179.0(2)

Catalytic Activities of Pincer Palladium Complexes for the Suzuki Coupling Reaction. As mentioned above, a variety of pincer palladium complexes are emerging as a new class of efficient catalysts for C−C bond forming reactions.[1] For example, the PCP pincer palladium complexes with phosphinito groups have been used as catalysts in the Heck reaction,[3a,c,5b,6] Suzuki coupling,[3b,5b] Stille coupling,[5b] Sonogashira coupling,[7] allylic alkylation,[5a] allylic stannylation,[3d] allylation of aldehydes and imines,[3e,8] and α-arylation of ketones.[9] To test the catalytic activities of the pincer complexes **5**, the Suzuki coupling reaction was carried out (Table 3).

The reaction of 4-bromoacetophenone (**6**) with phenylboronic acid (**7**) took place in the presence of 0.1−0.01 mol % of the pincer complexes **5** to give 4-acetylbiphenyl (**8**). The turnover numbers (TONs) of the pincer complexes **5** were 328−5790[10] and were highly dependent on the substituents at the phosphorus atom. The diphenyl derivative **5a** showed the highest catalytic activity of the pincer complexes **5**.

Table 3. Suzuki Coupling Reaction of 4-Bromoacetophenone with Phenylboronic Acid Catalyzed by Pincer Complexes 5[a]



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entry	**5**	**5** (mol %)	yield (%)	TON
1	**5a**	0.01	58	5790
2	**5b**	0.1	60	599
3	**5c**	0.01	41	4050
4	**5d**	0.1	33	328
5	**5e**	0.01	20	2040
6	**5f**	0.1	60	603

[a] The reaction was carried out with 4-bromoacetophenone (**6**) (1.0 mmol), phenylboronic acid (**7**) (1.5 mmol), K_2CO_3 (2.0 mmol), and pincer complex **5** (0.1−0.01 mol %) under reflux in toluene (3.0 mL) for 24 h.

Conclusion

In summary, we have developed a new efficient synthetic route for the PCP pincer palladium complexes that is complementary to the nucleophilic ligand introduction routes. A variety of pincer complexes were successfully synthesized via the electrophilic ligand introduction route, in which the palladium−carbon bond was initially formed, and the electrophilic ligand moieties were introduced to the nucleophilic hydroxy groups. X-ray molecular structure analyses of the pincer complexes showed that they adopted square-planar geometries. The pincer complexes were active catalysts for the Suzuki coupling reaction, and their catalytic activities were dependent on the substituents at the phosphorus atom. Further applications of the ligand introduction route to the synthesis of other types of pincer complexes are underway and will be reported in due course.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. NMR spectra were recorded on a JEOL JNM-A500 spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C, 202 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^1H NMR. Chemical shifts of ^{13}C NMR are given relative to $CDCl_3$ as an internal standard (δ 77.0). The ^{31}P NMR data are reported relative to external 85% H_3PO_4. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ at 25 °C. ESI mass spectra were recorded on a JEOL JMS-T100LC spectrometer. Melting points were determined using a Yanaco MP-J3 micro melting point apparatus and are uncorrected. The IR spectrum was obtained using a JASCO FT/IR-460plus spectrophotometer in ATR mode. Dehydrated dichloromethane and toluene were purchased. Silica gel 60 from a commercial supplier was used in column chromatography. Commercially available reagents were used without purification. 2-Iodoresorcinol[11] and tetrakis(tri-

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phenylphosphine)palladium[12] were prepared according to procedures in the literature.

Synthesis of *trans*-(2,6-Dihydroxyphenyl)iodobis(triphenylphosphine)palladium (4). To a suspension of tetrakis(triphenylphosphine)palladium (5.78 g, 5.00 mmol) in dichloromethane (100 mL) was added 2-iodoresorcinol (**3**) (1.19 g, 5.03 mmol) at 25 °C, and the mixture was stirred at that temperature for 2 h. After the solvent was removed, the residue was purified by column chromatography on silica gel using hexane/ethyl acetate as an eluent to give *trans*-(2,6-dihydroxyphenyl)iodobis(triphenylphosphine)-palladium (**4**) (3.48 g, 4.01 mmol, 80%) as a pale yellow solid. Mp: 148−150 °C (dec). MS (ESI): *m*/*z* 739 ([M − I]$^+$). ^{1}H NMR ($CDCl_3$): δ 4.71 (s, 2H, OH), 5.49 (d, J = 7.9 Hz, 2H, Ar−H), 6.27 (t, J = 7.9 Hz, 1H, Ar−H), 7.25 (t, J = 6.9 Hz, 12H, Ar−H), 7.33 (t, J = 6.9 Hz, 6H, Ar−H), 7.56 (q, J = 6.9 Hz, 12H, Ar−H). ^{13}C{^{1}H} NMR: δ 106.8 (Ar), 126.9 (Ar), 127.8 (virtual t, J = 5.2 z, Ar), 130.0 (Ar), 131.7 (virtual t, J = 24.8 Hz, Ar), 134.6 (virtual t, J = 6.2 Hz, Ar), 155.6 (Ar). ^{31}P{^{1}H}NMR: δ 18.8. Anal. Calcd for $C_{42}H_{35}IO_2P_2Pd\cdot CH_3CO_2C_2H_5$ (955.10): C, 57.85; H, 4.54. Found: C, 57.77; H, 4.42. IR (ATR mode): ν(OH) 3371 cm^{-1}.

Synthesis of 2,6-Bis(diphenylphosphinoxy)phenyliodopalladium (5a). To a suspension of *trans*-(2,6-dihydroxyphenyl)iodobis-(triphenylphosphine)palladium (**4**) (217 mg, 0.250 mmol) in toluene (2.5 mL) was added triethylamine (55.7 mg, 0.550 mmol) at 0 °C. To the mixture was added chlorodiphenylphosphine (121 mg, 0.550 mmol) at 0 °C, and the mixture was stirred at 25 °C for 1 h. The reaction mixture was poured into water (10 mL) and extracted with chloroform (10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give 2,6-bis-(diphenylphosphinoxy)phenyliodopalladium (**5a**) (163 mg, 0.229 mmol, 92%) as a pale yellow solid. Mp: >300 °C. MS (ESI): *m*/*z* 583 ([M − I]$^+$). ^{1}H NMR ($CDCl_3$): δ 6.79 (d, J = 7.9 Hz, 2H, Ar−H), 7.12 (t, J = 7.9 Hz, 1H, Ar−H), 7.45−7.52 (m, 12H, Ar−H), 8.00 (q, J = 6.3 Hz, 8H, Ar−H). ^{13}C{^{1}H} NMR: δ 106.9 (virtual t, J = 7.8 Hz, Ar), 128.8 (virtual t, J = 5.7 Hz, Ar), 129.0 (Ar), 132.0 (Ar), 132.4 (virtual t, J = 8.3 Hz, Ar), 133.4 (virtual t, J = 25.9 Hz, Ar), 137.7 (Ar), 164.2 (virtual t, J = 7.8 Hz, Ar). ^{31}P{^{1}H} NMR: δ 144.0. Anal. Calcd for $C_{30}H_{23}IO_2P_2Pd$ (710.77): C, 50.69; H, 3.26. Found: C, 50.40; H, 3.30.

2,6-Bis[bis(2-methylphenyl)phosphinoxy]phenyliodopalladium (5b). Yield: 92% (176 mg, 0.229 mmol), pale yellow solid. Mp: 294−296 °C. MS (ESI): *m*/*z* 639 ([M − I]$^+$). ^{1}H NMR ($CDCl_3$): δ 2.48 (s, 12H, CH_3), 6.68 (d, J = 7.9 Hz, 2H, Ar−H), 7.08 (t, J = 7.9 Hz, 1H, Ar−H), 7.24−7.29 (t, J = 7.4 Hz, 8H, Ar−H), 7.42 (t, J = 7.4 Hz, 4H, Ar−H), 7.95 (q, J = 7.4 Hz, 4H, Ar−H). ^{13}C{^{1}H} NMR: δ 22.5 (CH_3), 106.9 (virtual t, J = 7.8 Hz, Ar), 125.9 (virtual t, J = 6.7 Hz, Ar), 128.9 (Ar), 130.4 (virtual t, J = 25.3 Hz, Ar), 131.8 (virtual t, J = 3.1 Hz, Ar), 132.4 (Ar), 135.2 (virtual t, J = 11.9 Hz, Ar), 138.9 (Ar), 141.9 (virtual t, J = 4.7 Hz, Ar), 163.6 (virtual t, J = 7.2 Hz, Ar). ^{31}P{^{1}H} NMR: δ 153.4. Anal. Calcd for $C_{34}H_{31}IO_2P_2Pd\cdot H_2O$ (784.90): C, 52.03; H, 4.24. Found: C, 52.30; H, 4.03.

2,6-Bis(diethylphosphinoxy)phenyliodopalladium (5c). Yield: 86% (112 mg, 0.216 mmol), colorless solid. Mp: 102−105 °C. MS (ESI): *m*/*z* 424 ([M − I + MeOH]$^+$). ^{1}H NMR ($CDCl_3$): δ 1.26−1.33 (td, J = 8.5, 17.1 Hz, 12H, CH_3), 2.21−2.31 (m, 8H, CH_2), 6.59 (d, J = 8.2 Hz, 2H, Ar−H), 7.03 (t, J = 8.2 Hz, 1H, Ar−H). ^{13}C{^{1}H} NMR: δ 8.0 (CH_3), 24.4 (virtual t, J = 14.0 Hz, CH_2), 106.1 (virtual t, J = 7.8 Hz, Ar), 128.5 (Ar), 136.2 (Ar), 165.3 (virtual t, J = 7.2 Hz, Ar). ^{31}P{^{1}H} NMR: δ 176.9. Anal. Calcd for $C_{14}H_{23}IO_2P_2Pd$ (518.60): C, 32.42; H, 4.47. Found: C, 32.34; H, 4.45.

2,6-Bis[bis(1-methylethyl)phosphinoxy]phenyliodopalladium (5d). Yield: 95% (137 mg, 0.237 mmol), colorless solid. Mp: 148−150 °C. MS (ESI): *m*/*z* 447 ([M − I]$^+$). ^{1}H NMR

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Table 4. Selected Crystallographic Data for Palladium Complexes 4 and 5a−f

	4	**5a**	**5b**	**5c**	**5d**	**5e**	**5f**
formula	$C_{43}H_{37}IO_2P_2PdCl_2$	$C_{30}H_{23}O_2IP_2Pd$	$C_{34}H_{31}IO_2P_2Pd$	$C_{14}H_{23}IO_2P_2Pd$	$C_{18}H_{31}IO_2P_2Pd$	$C_{30}H_{47}IO_2P_2Pd$	$C_{22}H_{43}IN_4O_2P_2Pd$
fw	951.92	710.76	766.87	518.59	574.69	734.95	690.86
cryst size, mm	0.10 × 0.15 × 0.10	0.20 × 0.20 × 0.20	0.25 × 0.25 × 0.10	0.30 × 0.25 × 0.20	0.20 × 0.25 × 0.25	0.25 × 0.25 × 0.20	0.15 × 0.15 × 0.10
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	*Pbcn* (No. 60)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	*Pccn* (No. 56)
a, Å	11.877(10)	16.616(3)	10.403(2)	29.0236(11)	8.343(2)	10.0692(11)	32.950(7)
b, Å	12.266(10)	10.991(2)	15.074(3)	14.3539(7)	12.441(3)	10.3890(11)	10.670(2)
c, Å	13.875(11)	16.714(3)	19.608(4)	13.7154(8)	22.069(5)	15.644(2)	16.740(4)
α, deg	90.175(12)				87.899(5)	94.457(5)	
β, deg	94.556(9)	117.461(2)	94.774(3)		83.911(5)	94.320(4)	
γ, deg	99.764(12)				82.008(5)	104.988(6)	
V, Å^3	1985.5(28)	2708.4(8)	3064.0(12)	5713.9(5)	2255.0(8)	1568.3(3)	5885.4(22)
Z	2	4	4	12	4	2	8
μ, mm^{-1}	1.496	1.970	1.748	2.763	2.343	1.703	1.813
F_{000}	948.00	1392.00	1520.00	3024.00	1136.00	744.00	2784.00
D_{calcd}, g cm^{-3}	1.592	1.743	1.662	1.808	1.693	1.556	1.559
no. of unique reflns	8433	6418	7051	7180	9485	6630	7414
no. of variables	497	348	392	310	495	372	322
R	0.104	0.030	0.069	0.040	0.032	0.041	0.093
R_w	0.123	0.045	0.091	0.037	0.042	0.059	0.081
GOF	1.247	0.992	1.392	0.544	0.714	0.969	1.006
max./min. Δ*ρ*, e Å^{-3}	4.47, −1.67	1.89, −0.69	1.76, −1.82	1.79, −1.50	0.94, −0.84	2.37, −0.77	1.31, −0.99

($CDCl_3$): δ 1.28 (q, J = 7.7 Hz, 12H, CH_3), 1.39 (q, J = 7.7 Hz, 12H, CH_3), 2.50 (heptet, J = 7.7 Hz, 4H, CH), 6.59 (d, J = 8.4 Hz, 2H, Ar−H), 7.00 (t, J = 8.4 Hz, 1H, Ar−H). $^{13}C\{^1H\}$ NMR: δ 16.7 (CH_3), 18.1 (virtual t, J = 3.1 Hz, CH_3), 29.3 (virtual t, J = 11.9 Hz, CH), 105.7 (virtual t, J = 7.2 Hz, Ar), 128.2 (Ar), 135.2 (Ar), 165.9 (virtual t, J = 6.2 Hz, Ar). $^{31}P\{^1H\}$ NMR: δ 187.7. Anal. Calcd for $C_{18}H_{31}IO_2P_2Pd$ (574.71): C, 37.62; H, 5.44. Found: C, 37.46; H, 5.41.

2,6-Bis(dicyclohexylphosphinoxy)phenyliodopalladium (5e). Yield: 82% (149 mg, 0.203 mmol), colorless solid. Mp: 201−203 °C. MS (ESI): m/z 607 ($[M - I]^+$). ^1H NMR ($CDCl_3$): δ 1.21−1.38 (m, 12H, CH_2), 1.55 (dq, J = 2.9, 12.4 Hz, 4H, CH_2), 1.69−1.75 (m, 8H, CH_2), 1.82 (d, J = 11.6 Hz, 8H, CH_2), 1.90 (d, J = 12.8 Hz, 4H, CH_2), 1.99 (d, J = 12.8 Hz, 4H, CH_2), 2.29 (tt, J = 2.9, 12.5 Hz, 4H, CH), 6.56 (d, J = 8.1 Hz, 2H), 6.98 (t, J = 8.1 Hz, 1H). $^{13}C\{^1H\}$ NMR: δ 25.8 (CH_2), 26.3 (virtual t, J = 5.2 Hz, CH_2), 26.5 (virtual t, J = 7.2 Hz, CH_2), 26.7 (CH_2), 27.7 (CH_2), 38.3 (virtual t, J = 11.9 Hz, CH), 105.6 (virtual t, J = 7.2 Hz, Ar), 128.1 (Ar), 135.2 (Ar), 165.8 (virtual t, J = 6.2 Hz, Ar). $^{31}P\{^1H\}$ NMR: δ 180.7. Anal. Calcd for $C_{30}H_{47}IO_2P_2Pd$ (734.96): C, 49.03; H, 6.45. Found: C, 48.85; H, 6.44.

2,6-Bis[bis(diethylamino)phosphinoxy]phenyliodopalladium (5f). Yield: 94% (162 mg, 0.234 mmol), colorless solid. Mp: 94−96 °C. MS (ESI): m/z 563 ($[M - I]^+$). ^1H NMR ($CDCl_3$): δ 1.13 (t, J = 6.8 Hz, 24H, CH_3), 3.21 (octet, J = 6.8 Hz, 8H, CH_2), 3.32 (octet, J = 6.8 Hz, 8H, CH_2), 6.57 (d, J = 7.8 Hz, 2H, Ar−H), 7.06 (t, J = 7.8 Hz, 1H, Ar−H). $^{13}C\{^1H\}$ NMR: δ 14.2 (CH_3), 40.3 (virtual t, J = 5.7 Hz, CH_2), 105.8 (virtual t, J = 8.8 Hz, Ar), 128.7 (Ar), 133.9 (virtual t, J = 2.6 Hz, Ar), 159.6 (virtual t, J = 9.8 Hz, Ar). $^{31}P\{^1H\}$ NMR: δ 146.0. Anal. Calcd for $C_{22}H_{43}IN_4O_2P_2Pd$ (690.87): C, 38.25; H, 6.27; N, 8.11. Found: C, 38.15; H, 6.20; N, 8.07.

General Procedure for the Suzuki Coupling Reaction. To a suspension of potassium carbonate (2.0 mmol) in toluene (3.0 mL) was added 4-bromoacetophenone (**6**) (1.0 mmol), phenylboronic acid (**7**) (1.5 mmol), and the pincer complex **5** (0.01 M solution in toluene, 10−100 μL, 1×10^{-3} to 1×10^{-4} mmol, 0.1−0.01 mol %). The mixture was stirred under reflux in toluene for 24 h and allowed to cool to 25 °C. The reaction mixture was poured into aqueous HCl (2 M, 10 mL) and extracted with chloroform (2×10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give 4-acetylbiphenyl (**8**).

X-ray Structure Determination. Single crystals of **4** and **5a**−**c** suitable for an X-ray diffraction study were grown by slow diffusion of hexane into the dichloromethane solution of **4**, *tert*-butyl methyl ether into the chloroform solution of **5a**, ethyl acetate into the chloroform solution of **5b**, and hexane into the ethyl acetate solution of **5c**, respectively. Single crystals of **5d** and **5f** were obtained by slow evaporation of ethyl acetate solution of **5d** and **5f**. Single crystals of **5e** were obtained by the recrystallization of **5e** from hot ethyl acetate. X-ray data for single crystals were collected on a Rigaku Saturn CCD area detector at −100 °C using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by heavy-atom Patterson methods (PATTY for **4**) or direct methods (SIR 92 for **5a**−**e**, SIR 97 for **5f**) and expanded using Fourier techniques (DIRDIF99). All non-hydrogen atoms except for C20 and C22 in **5f** were refined anisotropically, and the hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package. Crystallographic data and details of structure refinement are summarized in Table 4.

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Supporting Information Available: CIF files giving crystallographic data for **4** and **5a**−**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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