pH-Dependent Cross-Coupling Reactions of Water-Soluble Organic Halides with Organoboron Compounds Catalyzed by the Organometallic Aqua Complex $[(SCS)Pd^{II}(H_2O)]^+$ ($SCS = C_6H_3$-2,6-$(CH_2SBu^t)_2$)

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This paper reports on the first example of pH-dependent cross-coupling reactions of water-soluble organic halides ($3\text{-}X(C_6H_4)CO_2H$, where X = Cl, Br, I) with organoboron compounds ($PhB(OH)_2$ and Ph_4BNa) to form $3\text{-}Ph(C_6H_4)CO_2H$, catalyzed by the mononuclear organometallic aqua complex $[(SCS)Pd^{II}(H_2O)]_2(SO_4)$ ($[\mathbf{1}]_2(SO_4)$, $SCS = C_6H_3$-2,6-$(CH_2SBu^t)_2$) in basic media ($8 < pH < 13$, $NaHCO_3/NaOH$ buffers). The structure of $\mathbf{1}(PF_6)$ was unequivocally determined by X-ray analysis. The reactions show unique pH selectivity depending upon the organoboron compounds; i.e., the rate of the reactions with $PhB(OH)_2$ shows a sharp maximum around pH 10, though the rate of the reactions with Ph_4BNa shows a flat maximum in a pH range of about 8−11. The pH dependence is discussed on the basis of the pK_a values of $[\mathbf{1}]_2(SO_4)$ and $PhB(OH)_2$.

Introduction

The chemistry of water-soluble organometallic complexes is presently undergoing very rapid growth because of many potential advantages, such as alleviation of environmental problems associated with the use of organic solvents, industrial applications (e.g., introduction of new biphasic processes), and reaction-specific pH selectivity.[1] Although the majority of these studies have been carried out with water-soluble organometallic complexes containing water-soluble phosphine ligands,[2,3] few have utilized organometallic complexes containing water molecules as ligands (i.e., organometallic aqua complexes).[4,5] These organometallic aqua complexes are expected to be new pH-selective catalysts, since their structures and properties drastically change as a function of pH due to deprotonation of the H_2O ligands. This has stimulated our interest in investigating unique pH-dependent catalytic reactions with the organometallic aqua complexes as catalysts in aqueous media.

Palladium-catalyzed cross-coupling reactions of organic halides with organoboron compounds (Suzuki coupling) are efficient methods for the construction of $C_{aryl}-C_{aryl}$ bonds in organic synthesis.[3,6,7] Herein, we report pH-dependent cross-coupling reactions of water-soluble organic halides ($3\text{-}X(C_6H_4)CO_2H$, where X = Cl, Br, I)[8] with organoboron compounds ($PhB(OH)_2$ and Ph_4BNa) to form $3\text{-}Ph(C_6H_4)CO_2H$ catalyzed by the mononuclear organometallic aqua complex $[(SCS)Pd^{II}(H_2O)]_2(SO_4)$ ($[\mathbf{1}]_2(SO_4)$, $SCS = C_6H_3$-2,6-$(CH_2SBu^t)_2$) in basic media ($8 < pH < 13$) (Scheme 1).

Results and Discussion

The New Organometallic Aqua Complex $[(SCS)Pd^{II}(H_2O)]^+$ (1). The tridentate SCS pincer ligand and

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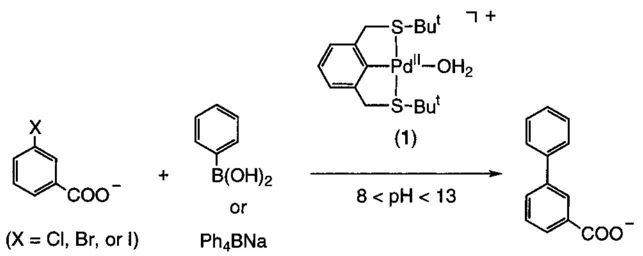
Scheme 1



[(SCS)Pd^{II}Cl] were prepared by the method described in ref 9. The complex [**1**]$_2$(SO$_4$) was synthesized from the reaction of [(SCS)Pd^{II}Cl] with Ag$_2$SO$_4$ in water under an air atmosphere (see Experimental Section). [**1**]$_2$(SO$_4$) has high solubility in water (400 mg/mL at 25 °C). The structure of **1**(PF$_6$) was determined by X-ray analysis.[10] As shown in Figure 1, complex **1** adopts distorted-square-planar coordination with one H$_2$O ligand. The Pd1–O1 bond length is 2.185(3) Å.

^{1}H NMR (Figure 2,[11] referenced to TSP,[12] 30 °C) and UV–vis experiments[13] (Figure 3) show that the pK_a value of [**1**]$_2$(SO$_4$) is 10.7; i.e., complex **1** is reversibly deprotonated to form the hydroxo complex [(SCS)Pd^{II}(OH)] (**2**) at pH 10.7 (eq 1). The positive-ion electrospray

$$[(SCS)Pd^{II}(H_2O)]^+ \xrightleftharpoons{pK_a = 10.7} [(SCS)Pd^{II}(OH)] + H^+ \tag{1}$$

ionization (ESI) mass spectrum of [**1**]$_2$(SO$_4$) dissolved in NaOH/H$_2$O at pH 12.5 shows a signal at *m*/*z* 427.2 (relative intensity (*I*) 48% in the *m*/*z* range 100–600, Figure 4a), which has a characteristic distribution of isotopomers (Figure 4b) that matches well with the calculated isotopic distribution for [**2** + Na]$^+$ (Figure 4c).[14] MS/MS measurements show that the signal denoted by a dagger at *m*/*z* 387.2 (*I* = 100%) is a product ion ([**2** – OH]$^+$) of [**2** + Na]$^+$.

Conditions of the Cross-Coupling Reactions. The pH-dependent cross-coupling reactions of water-soluble organic halides (3-X(C$_6$H$_4$)CO$_2$H, where X = Cl, Br, I, 100 μmol) with organoboron compounds (PhB(OH)$_2$, 100 μmol; Ph$_4$BNa, 25 μmol) catalyzed by [**1**]$_2$(SO$_4$) (0.5 μmol) in water (1.1 mL) were investigated at 40–100 °C. The reactions can be carried out under an air atmosphere because the catalyst **1** is not sensitive to O$_2$.[15] It is important to note that there is no formation of metallic palladium under the conditions of this study. To maintain the pH of the solution during the reaction, NaHCO$_3$/NaOH buffers were used (see Experimental Section). It was confirmed that the pH of the solution does not change in the course of the reaction. The

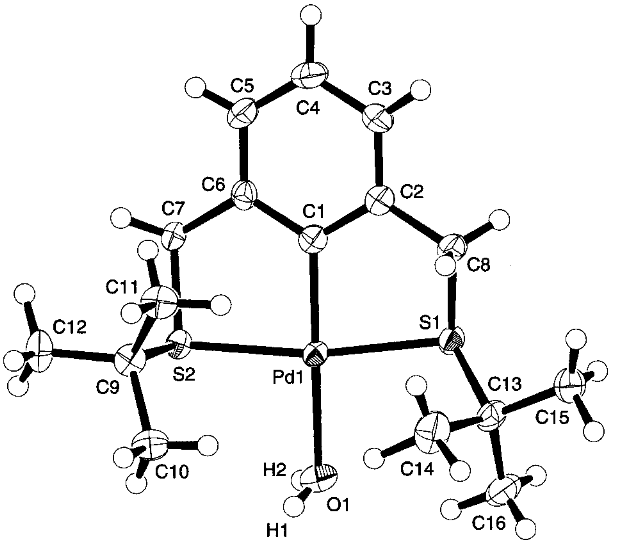


Figure 1. ORTEP drawing of **1**(PF$_6$). The anion (PF$_6$) is omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1–O1 = 2.185(3), Pd1–S1 = 2.306(1), Pd1–S2 = 2.306(1), Pd1–C1 = 1.964(4); S1–Pd–S2 = 170.10(4), S1–Pd1–C1 = 84.2(1), S2–Pd1–C1 = 86.1(1), S1–Pd1–O1 = 96.4(1), S2–Pd1–O1 = 93.1(1), O1–Pd1–C1 = 173.2(2).

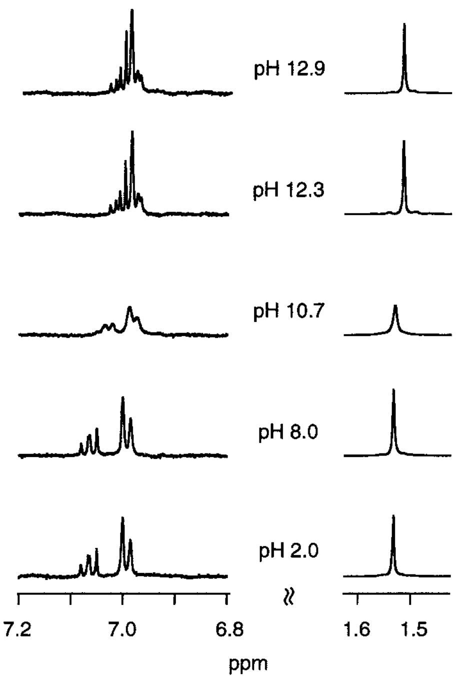


Figure 2. pH-dependent ^{1}H NMR spectra of **1** in a pH range of about 2.0–12.9. Experiments were performed by dissolving [**1**]$_2$(SO$_4$) (2.5 μmol) in H$_2$O (1 mL) at 30 °C. The pH of the solution was adjusted by using 0.1–5 M H$_2$SO$_4$/H$_2$O and 0.1–5 M NaOH/H$_2$O.

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[10] Crystal data for **1**(PF$_6$): C$_{16}$H$_{27}$F$_6$OPPdS$_2$, MW 550.87, monoclinic, space group *Pc* (No. 7), a = 8.590(3) Å, b = 10.930(3) Å, c = 11.4900(7) Å, β = 92.490(1)°, V = 1077.8(5) Å^3, Z = 2, D_c = 1.697 g cm^{-3}, μ(Mo Kα) = 11.84 cm^{-1}, R = 0.031, and R_w = 0.062. The crystal structure of **1**(PF$_6$) reveals hydrogen bonds between the aqua ligand of **1** and the counteranion (PF$_6^-$). Crystallographic data for **1**(PF$_6$) have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC-172019. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

[11] The ^{1}H NMR signals at pH 10.7 are broadened. This reflects the existence of aqua and hydroxo complexes in rapid equilibrium.

[12] TSP = 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt.

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[14] It was confirmed that the sodium ion of [**2** + Na]$^+$ is derived from the solution of NaOH/H$_2$O by the same ESI-MS experiments in KOH/H$_2$O; i.e., the positive-ion ESI mass spectrum of **2** dissolved in KOH/H$_2$O at pH 12.5 shows a signal at *m*/*z* 443.2 corresponding to [**2** + K]$^+$.

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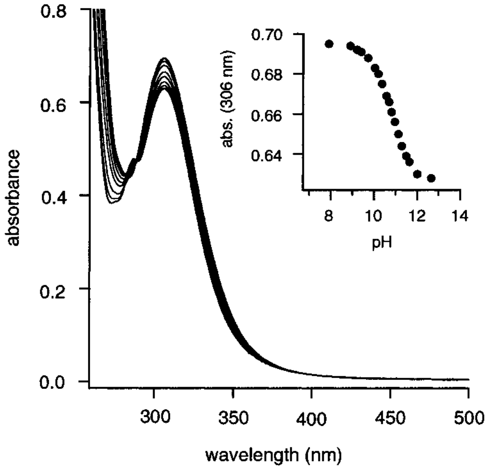

Figure 3. pH-dependent UV–vis spectra of $[\mathbf{1}]_2(SO_4)$ in a pH range of about 7.0–13.0. The inset gives a plot of absorbance (λ = 306 nm) vs pH. Experiments were performed by the titration of $[\mathbf{1}]_2(SO_4)$ (1×10^{-4} M) with 0.1–5 M $NaOH/H_2O$ at 30 °C.

turnover number (TON) is expressed as the number of moles of product formed per mole of catalyst **1**. The TONs were determined by ^1H NMR analysis of the reaction mixture samples (based on the organic halides and the product).

pH-Dependent Cross-Coupling Reactions. The reactions show unique pH selectivity depending upon the organoboron compounds. The rate of the reactions with $PhB(OH)_2$ shows a sharp maximum around pH 10, though the rate of the reactions with Ph_4BNa shows a flat maximum in a pH range of about 8–11 (Figure 5). The pH dependence could be rationalized as follows. (i) The pK_a value of $[\mathbf{1}]_2(SO_4)$ is 10.7; thus, above pH 10.7, the catalyst **1** is predominantly deprotonated to form the catalytically inactive hydroxo complex **2**. (ii) The pK_a value of $PhB(OH)_2$ is 8.8 (eq 2);[16] thus, below pH 8.8, the reactive phenyl hydroxyboronate anion $PhB(OH)_3^-$ is transformed to the unreactive free phenyl boronic acid $PhB(OH)_2$.[17]

$$\mathrm{PhB(OH)_2 + H_2O \overset{pK_a = 8.8}{\rightleftharpoons} PhB(OH)_3^- + H^+} \tag{2}$$

As shown in Table 1, the reactions of the water-soluble organic chloride $3\text{-}Cl(C_6H_4)CO_2H$ with the organoboron compounds do not provide the product under the present conditions (entries 1 and 2). However, the reactions of $3\text{-}X(C_6H_4)CO_2H$ (X = Br, I) with the organoboron compounds catalytically yield the product $3\text{-}Ph\text{-}(C_6H_4)CO_2H$ (entries 3–6). Thus, the reactivity of the aryl halides ($3\text{-}X(C_6H_4)CO_2H$) shows the typical order: $X = I > Br \gg Cl$.[3,6,7] When the organoboron compound is changed from $PhB(OH)_2$ to Ph_4BNa, the TONs are considerably increased (entries 3–6). The catalytic activity is observed with 1–0.001 mol % catalyst **1** (entries 7–10). The rate of the reactions is dependent on the reaction times (Figure 6) and temperature (entries 7–10). At higher temperatures, therefore, we can decrease the amount of the catalyst **1** to obtain TONs of up to 8.5×10^4 at 100 °C after 12 h (entry 11).

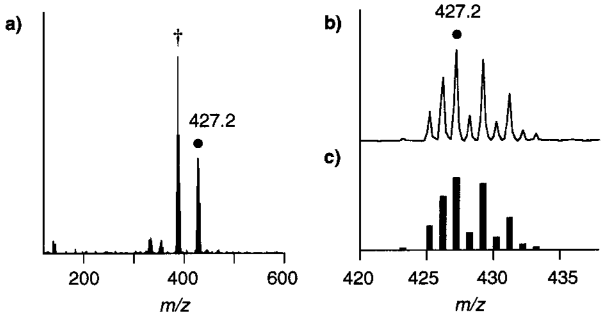

Figure 4. (a) Positive-ion ESI mass spectrum of $[\mathbf{1}]_2(SO_4)$ dissolved in $NaOH/H_2O$ at pH 12.5. The signal at *m/z* 427.2 corresponds to $[\mathbf{2} + Na]^+$. The signal denoted with a dagger at *m/z* 387.2 is a product ion ($[\mathbf{2} - OH]^+$) of $[\mathbf{2} + Na]^+$. (b) The signal at *m/z* 427.2. (c) Calculated isotopic distribution for $[\mathbf{2} + Na]^+$.

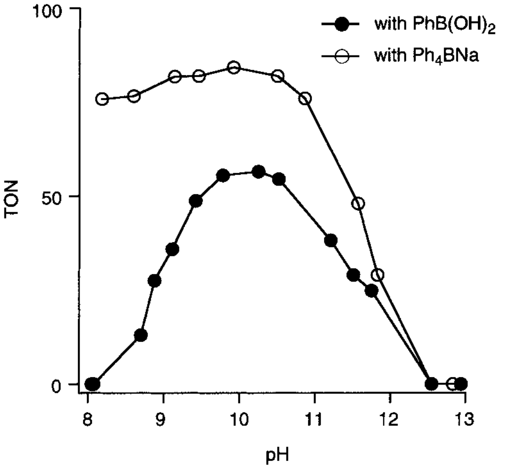

Figure 5. Typical pH-dependence profile of the cross-coupling reaction of $3\text{-}I(C_6H_4)CO_2H$ with $PhB(OH)_2$ or Ph_4BNa. Conditions: **1** (1 mol %), $I(C_6H_4)CO_2H$ (100 μmol), $PhB(OH)_2$ (100 μmol), Ph_4BNa (25 μmol), $NaHCO_3/NaOH$ buffers (1.1 mL) prepared by 1 M $NaHCO_3/H_2O$ and 5 M $NaOH/H_2O$, 40 °C, 6 h.

In addition, it was confirmed that the catalyst **1** can be reused at least three times; i.e., upon addition of more substrates after the reaction, the catalytic cycle is resumed (Figure S1 in the Supporting Information), though the catalyst **1** was gradually deactivated. However, it is noteworthy that formation of metallic palladium was not observed after the reactions.

Conclusions

We have demonstrated the potential of the organometallic aqua complex **1** to be a pH-selective catalyst for the cross-coupling reactions of water-soluble organic halides with organoboron compounds in the basic media ($8 < pH < 13$). The reactions show unique pH selectivity depending upon the organoboron compounds; i.e., the rate of the reactions with $PhB(OH)_2$ shows a sharp maximum around pH 10, though the rate of the reactions with Ph_4BNa shows a flat maximum in a pH range of about 8–11. The pH dependence was discussed on the basis of the pK_a values of $[\mathbf{1}]_2(SO_4)$ and $PhB(OH)_2$.

Experimental Section

Materials and Methods. All experiments were carried out under an air atmosphere. Phenylboronic acid ($PhB(OH)_2$) and

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[16] Brown, R. D.; Buchanan, A. S.; Humffray, A. A. *Aust. J. Chem.* **1965**, *18*, 1527–1538.

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Table 1. Cross-Coupling Reactions of Water-Soluble Organic Halides with Organoboron Compounds To Form 3-$PhC_6H_4CO_2H$ Catalyzed by the Organometallic Aqua Complex 1 in Water at pH 9.5[a]

entry	X of 3-$X(C_6H_4)CO_2H$	organoboron	amt of complex **1** (mol %)	*T* (°C)	*t* (h)	yield (%)	TON[b]	TOF[c]
1	Cl	$PhB(OH)_2$	1	40	6	0	0	0
2	Cl	Ph_4BNa	1	40	6	0	0	0
3	Br	$PhB(OH)_2$	1	40	6	18	18	3
4	Br	Ph_4BNa	1	40	6	68	68	11
5	I	$PhB(OH)_2$	1	40	6	49	49	8
6	I	Ph_4BNa	1	40	6	82	82	14
7	I	Ph_4BNa	1	40	1	50	50	50
8	I	Ph_4BNa	0.2	60	1	66	330	330
9	I	Ph_4BNa	0.05	80	1	65	1300	1300
10	I	Ph_4BNa	0.001	100	1	46	46000	46000
11	I	Ph_4BNa	0.001	100	12	85	85000	7083
12	I	$PhB(OH)_2$	1	60	18	100	100	6
13	I	Ph_4BNa	1	60	12	100	100	8

[a] Conditions: organic halide (100 μmol), $PhB(OH)_2$ (100 μmol), Ph_4BNa (25 μmol), $NaHCO_3/NaOH$ buffer (1.1 mL, pH 9.5) prepared by 1 M $NaHCO_3/H_2O$ and 5 M $NaOH/H_2O$. [b] TON: turnover number ((mol of product)/(mol of catalyst)), determined by ^1H NMR analysis of the reaction mixture samples (based on the organic halides and the product). [c] TOF: turnover frequency (mol of product/((mol of catalyst) time)).

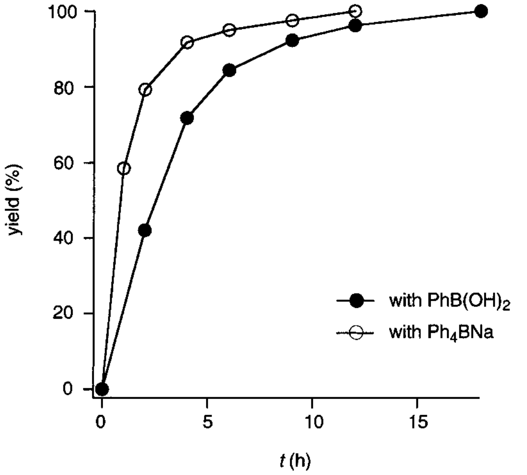

Figure 6. Time course of TON of the cross-coupling reaction of 3-$I(C_6H_4)CO_2H$ with $PhB(OH)_2$ or Ph_4BNa. Conditions: **1** (1 mol %), $I(C_6H_4)CO_2H$ (100 μmol), $PhB(OH)_2$ (100 μmol), Ph_4BNa (25 μmol), $NaHCO_3/NaOH$ buffer (1.1 mL, pH 9.5) prepared by using 1 M $NaHCO_3/H_2O$ and 5 M $NaOH/H_2O$, 60 °C.

3-bromobenzoic acid (3-$Br(C_6H_4)CO_2H$) (highest purity available) were purchased from Aldrich Chemicals Co. and sodium tetraphenylborate (Ph_4BNa), 3-iodobenzoic acid (3-$I(C_6H_4)CO_2H$), and 3-chlorobenzoic acid (3-$Cl(C_6H_4)CO_2H$) (highest purity available) from Tokyo Kasei Kogyo Co., Ltd.; these reagents were used as received. Purification of water (18.2 MΩ cm) was performed with the Milli-Q system (Millipore; Milli-RO 5 plus and Milli-Q plus). The ^1H NMR spectra were recorded on a JEOL JNM-LA 500 spectrometer or a JEOL JNM-EX 270 spectrometer. UV−vis spectra were recorded on a Shimadzu UV-2400 spectrophotometer. ESI-MS data were obtained by an API 300 triple-quadrupole mass spectrometer (PE-Sciex) in the positive detection mode, equipped with an ion spray interface. The sprayer was held at a potential of 4.5 kV, and compressed N_2 was employed to assist liquid nebulization. The orifice potential was maintained at 25 V. Elemental analyses were performed with a Yanako CHN corder MT-6.

pH Adjustment. In the pH range 1−13, the pH of the solution was determined by a pH meter (TOA; HM-5A) equipped with a glass electrode (TOA; GS-5015C) or a pH meter (IQ Scientific Instruments, Inc.; IQ 200) equipped with a stainless micro pH probe (IQ Scientific Instruments, Inc.; PH15-SS). To determine the exact pH values, the ^1H NMR experiments were performed by using an NMR tube (diameter 5.0 mm) with a sealed capillary tube (diameter 1.5 mm) containing 10 μL of 500 mM TSP[11] (as the reference with the methyl proton resonance set at 0.00 ppm) dissolved in D_2O (for deuterium lock). In the experiments determining the pH-dependent structural change of **1** by ^1H NMR, UV−vis, and ESI-MS, the pH of the solution was adjusted by using 0.1−5 M H_2SO_4/H_2O and 0.1−5 M $NaOH/H_2O$ without buffer. To maintain the pH of the solution during the cross-coupling reactions, $NaHCO_3/NaOH$ buffers prepared by 1 M $NaHCO_3/H_2O$ and 5 M $NaOH/H_2O$ were used.

$[(SCS)Pd^{II}(H_2O)]_2(SO_4)$ ($[\mathbf{1}]_2(SO_4)$). A solution of $[(SCS)Pd^{II}Cl]$ (300 mg, 0.7 mmol) and Ag_2SO_4 (110 mg, 0.35 mmol) in H_2O (50 mL, solution pH ca. 8.0) was stirred at ambient temperature for 24 h under an air atmosphere, and the precipitating AgCl was removed by filtration. The solvent was evaporated to yield a yellow powder of $[\mathbf{1}]_2(SO_4)$, which was dried in vacuo (yield 90% based on $[(SCS)Pd^{II}Cl]$). ^1H NMR (500 MHz, in H_2SO_4/H_2O at pH 2.0, referenced to TSP, 30 °C): δ 1.53 (s, 18H, Bu^t), 4.28 (s, 4H, CH_2), 6.99 (d, $J = 7.5$ Hz, 2H, CH aromatic), 7.07 (t, $J = 7.5$ Hz, 1H, CH aromatic). ESI-MS (in H_2SO_4/H_2O at pH 2.5): *m/z* 387.2 ($[\mathbf{1} - H_2O]^+$, relative intensity (I) = 100% in the *m/z* range 100−600). UV−vis (in H_2SO_4/H_2O at pH 2.0, 30 °C; λ_{max} (nm), ϵ ($M^{-1}cm^{-1}$)): 306, 6960. Anal. Calcd for $C_{32}H_{54}O_6Pd_2S_5$: C, 42.33; H, 5.99. Found: C, 41.94; H, 5.73.

X-ray Crystallographic Analysis. To the solution of $[\mathbf{1}]_2(SO_4)$ in water was added NH_4PF_6, giving a yellow powder of $\mathbf{1}(PF_6)$, which was collected by filtration. Yellow crystals of $\mathbf{1}(PF_6)$ used in the X-ray structure analysis were obtained from a CH_2Cl_2 solution of $\mathbf{1}(PF_6)$. Measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp. Crystal data, data collection parameters, structure solution and refinement details, atomic coordinates, anisotropic displacement parameters, bond lengths, and bond angles are given in the Supporting Information.

Typical Procedure for the Cross-Coupling Reactions (e.g., for Entry 6 in Table 1). Phenylboronic acid (13 mg 100 μmol) and 3-iodobenzoic acid (25 mg, 100 μmol) were dissolved in $NaHCO_3/NaOH$ buffers (1 mL, pH 9.5) under an air atmosphere. Then, 5 mM $[\mathbf{1}]_2(SO_4)/H_2O$ (100 μL, 0.5 μmol (1 mol % of **1**)) was added. The mixture was vigorously stirred for 6 h at 40 °C. After it was cooled, the resulting mixture was analyzed by ^1H NMR. 3-Phenylbenzoic acid can be easily isolated from the reaction mixture by the method described in ref 7b.

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Supporting Information Available: A figure giving details of the catalytic reactions and tables giving crystallographic information (13 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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