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(β-Oxoiminato)(phosphanyl)palladium Complexes as Highly Active Catalysts in Suzuki–Miyaura Coupling Reactions

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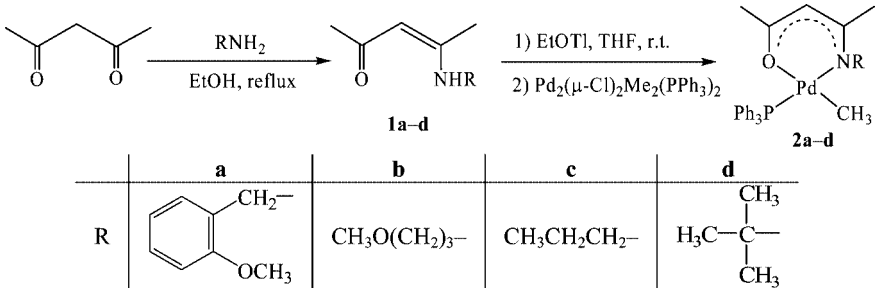
(β-Oxoiminato)(phosphanyl)palladium complexes have been used as catalysts in Suzuki–Miyaura coupling reactions. In the presence of these palladium complexes, various aryl iodides and bromides were efficiently coupled with phenylboronic acid with extremely high turnover frequencies under mild conditions. Furthermore, the catalyst system was also found to be effective in the reactions of aryl chlorides. This work indicates that these palladium complexes can serve as highly active catalysts in Suzuki–Miyaura reactions.

Introduction

Metal-catalyzed coupling reactions have been recognized as convenient one-step methods for the construction of carbon–carbon bonds.[1] Among them, the Suzuki–Miyaura coupling reaction of aryl halides with arylboronic acids represents one of the synthetically most valuable methods for the synthesis of biaryl derivatives in recent decades.[2] Phosphane ligands have been outstanding in the palladium-catalyzed coupling reaction. Sterically bulky monophosphanes,[3] diphosphanes,[4] electron-rich trialkylphosphanes,[5] phosphites,[6] and cyclopalladated phosphanes[7] have been proven to be excellent ligands for Suzuki–Miyaura reactions. However, many (phosphane)palladium complexes are sensitive to air and moisture at elevated temperatures, the Pd catalyst suffering deactivation in the reaction. Considerable work has been focused on this reaction in an effort to achieve a higher degree of efficiency under mild conditions. The search for new catalysts that exhibit high activity and stability with a broad range of substrates is still one of the most significant challenges in the coupling reaction. In this context, we envisioned (β-oxoiminato)-(phosphanyl)palladium complexes **2** as catalysts for the Suzuki reaction. β-Oxoimines have drawn much interest in coordination chemistry due to their resonance stability and unique structures.[8] Furthermore, the electronic and steric properties of β-oxoimine ligands can be partially controlled by changing the substituent on the N atom.[9] β-Oxoiminato complexes have been widely used as precursors in metallorganic chemical vapor deposition.[10] In contrast, their use as catalysts is limited to olefin polymerization.[11] To the best of our knowledge, no (β-oxoiminato)palladium complexes have been utilized as catalysts in the Suzuki–Miyaura reaction. Thus, it was of interest to explore their catalytic ability in this coupling reaction. Herein, we describe the synthesis of the (β-oxoiminato)(phosphanyl)palladium(II) complexes and their significant application in the Suzuki–Miyaura reaction.



Scheme 1. Synthesis of (β-oxoiminato)(phosphanyl)palladium complexes **2**.

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Results and Discussion

The Pd catalysts were easily prepared from commercially available 2,4-pentanedione and primary amines in a three-step synthesis (Scheme 1). Schiff-base condensation of 2,4-pentanedione and primary amines in refluxing ethanol gave the corresponding β-oxoimines **1a**–**d** in high yields. Deprotonation of **1** with EtOTl in THF followed by treatment with $[Pd_2(PPh_3)_2Me_2(\mu\text{-}Cl)_2]$[12] led to the formation of the corresponding Pd complexes **2**. Interestingly, the use of EtOTl[13] instead of conventional strong bases such as NaH, KH, MeONa, and BuLi was found to be more effective for the formation of the Pd complexes. The complexes were characterized by NMR spectra and elemental analyses. Fortunately, a single crystal of **2a** for X-ray structure determination was obtained by recrystallization from a hexane/dichloromethane (10:1) solution. Figure 1 shows the molecular structure of **2a** and selected bond lengths and angles. In the crystal structure, the palladium atom is in a slightly distorted square-planar environment with the β-oxoiminato backbone, triphenylphosphane ligand, and methyl group. The Pd–N(1) distance (2.117 Å) is longer than the Pd–O(1) distance (2.060 Å) which may be ascribed to the presence of the bulky 2-methoxybenzyl substituent on the N atom. As expected from the small coupling constant $J_{P\text{-}Me}$ (3.2 Hz) and the chelating nature of the β-oxoiminato ligand, the triphenylphosphane ligand is located *cis* to the methyl group. Additionally, the oxygen atom on the pendant 2-methoxybenzyl substituent of **2a** is uncoordinated.

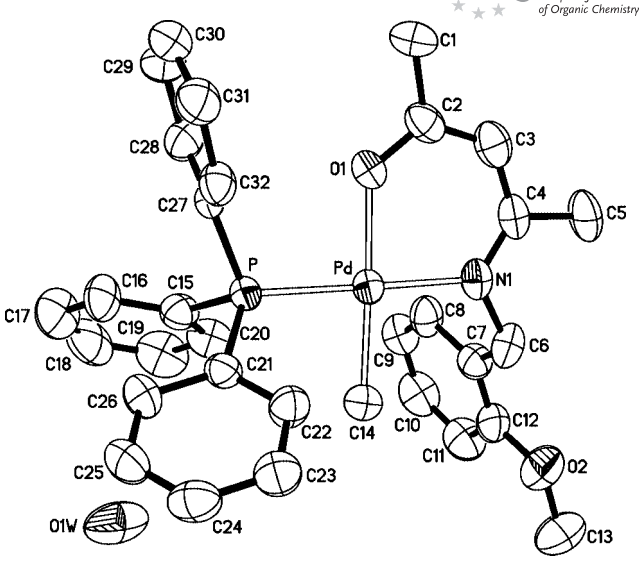
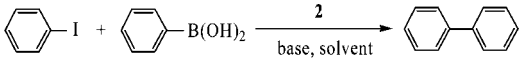


Figure 1. X-ray molecular structure of Pd complex **2a**. Selected bond lengths [Å] and angles [°]: Pd–C(14) 2.051(6), Pd–O(1) 2.060(4), Pd–N(1) 2.116(5), Pd–P 2.2418(15); C(14)–Pd–O(1) 175.5(3), C(14)–Pd–P 87.5(2), C(14)–Pd–N(1) 92.6(2), O(1)–Pd–P 89.07(13), O(1)–Pd–N(1) 90.92(19), N(1)–Pd–P 177.17(14).

With the Pd catalyst **2** in hand, we first tested the Suzuki–Miyaura coupling reaction of iodobenzene with phenylboronic acid in the presence of Na_2CO_3 as a model reaction. The reaction in DMA/H_2O (1:1) was initially performed with 0.01 mol-% of **2**. The reaction proceeded at

Table 1. Suzuki–Miyaura coupling of iodobenzene with phenylboronic acid.[a]



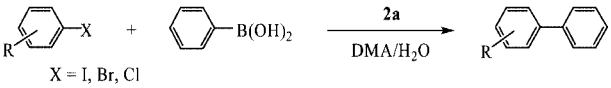
Entry	Solvent	**2** (Cat. loading [mol-%])	Base	*T* [°C]	Time [h]	Yield [%][b]
1	DMA/H_2O	**2a** (0.01)	Na_2CO_3	65	0.5	99 (95)
2	DMF/H_2O	**2a** (0.01)	Na_2CO_3	65	0.5	97
3	DMSO/H_2O	**2a** (0.01)	Na_2CO_3	65	0.5	98
4	EtOH/H_2O	**2a** (0.01)	Na_2CO_3	65	0.7	93 (90)
5	MeOH/H_2O	**2a** (0.01)	Na_2CO_3	65	0.7	95
6	DMA/H_2O	**2a** (0.01)	Na_2OAc	65	0.6	91
7	DMA/H_2O	**2a** (0.01)	K_2CO_3	65	0.5	94
8	DMAH_2O	**2a** (0.01)	K_3PO_4	65	0.5	97
9	DMA/H_2O	**2a** (0.001)	Na_2CO_3	65	2	92 (86)
10	DMA/H_2O	**2a** (0.0001)	Na_2CO_3	65	10	90
11	DMA/H_2O	**2a** (0.01)	Na_2CO_3	50	1	96
12	DMA/H_2O	**2a** (0.01)	Na_2CO_3	40	1	92
13	DMA/H_2O	**2a** (0.01)	Na_2CO_3	25	8	80
14	DMA/H_2O	**2b** (0.01)	Na_2CO_3	65	0.7	97 (93)
15	DMA/H_2O	**2b** (0.01)	Na_2CO_3	40	1.5	92
16	EtOH/H_2O	**2b** (0.01)	Na_2CO_3	65	1	95
17	DMA/H_2O	**2c** (0.01)	Na_2CO_3	65	1	90 (83)
18	DMA/H_2O	**2c** (0.01)	Na_2CO_3	40	1.5	82
19	EtOH/H_2O	**2c** (0.01)	Na_2CO_3	65	1	89
20	DMA/H_2O	**2d** (0.01)	Na_2CO_3	65	1	88
21	DMA/H_2O	**2d** (0.01)	Na_2CO_3	40	1.5	70
22	EtOH/H_2O	**2d** (0.01)	Na_2CO_3	65	1	86

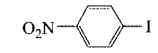
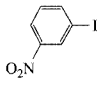
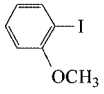
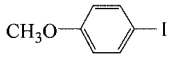
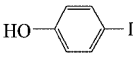
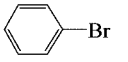
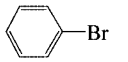
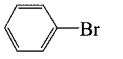
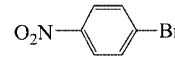
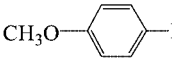
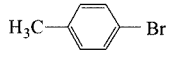
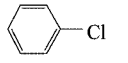
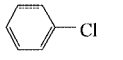
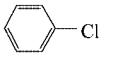
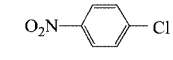
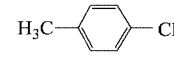
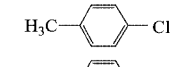
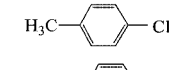
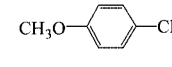
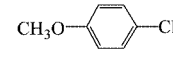
[a] Reactions were performed with a molar ratio of iodobenzene/phenylboronic acid/base = 1.0:1.1:2.0 in 50% aqueous solvent. [b] The yield was determined by GC using *n*-dodecane as the internal standard and based on the amount of iodobenzene employed. The isolated yield is given in parentheses.

65 °C to completion within 0.5 h, and all of the starting material was converted into the product (Table 1, Entry 1). The effect of solvent on the activity of **2a** was examined with different polar solvents. When the reaction was conducted in aqueous DMF, DMSO, EtOH, and MeOH instead of aqueous DMA similar results were obtained under the same conditions (Entries 2–5). It is interesting that the reactions in aqueous ethanol and methanol gave excellent results. Parameters such as base, catalyst loading, and reaction temperature were also surveyed. Na_2CO_3 as a base gave slightly better results than Na_2OAc, K_2CO_3, and K_3PO_4 (Entries 6–8). When the loading of **2a** was reduced to 0.001 mol-%, the high conversion was still maintained (Entry 9). Furthermore, the reaction was also successful with a lower catalytic loading of 0.0001 mol-%; an ultrahigh TOF of 9×10^6 h^{-1} was obtained for the coupling reaction (Entry 10). Catalyst **2a** showed outstanding performance at low temperatures (25–50 °C, Entries 11–13). It is noteworthy that the catalyst **2a** shows outstanding performance even at 25 °C (Entry 13). Further optimization of the reaction conditions was not attempted to obtain higher TOFs. The presence of water appears to be necessary in mild conditions due to the low solubility of Na_2CO_3 in organic solvents. The complex is very stable to oxygen and moisture; little change in its activity was observed in the coupling when the Pd complex was exposed to air and water. Pd complexes **2b**–**d** were also examined in the coupling reaction of iodobenzene with phenylboronic acid (Entries 14–22). Substituents on the N atom have a meaningful effect on the activity. Complex **2b** has a similar catalytic activity to **2a** at 40 °C (Entry 15). In contrast, the use of catalysts **2c** and **2d** caused a reduction in the rate under the same conditions (Entries 18 and 21). Complexes **2a** and **2b** with an alkoxyalkyl group on the N atom seem to be more effective catalysts than **2c** and **2d** with an alkyl group. This result indicates that the alkoxyalkyl group as well as the triphenylphosphane ligand contribute to the catalytic activity of the ligands. The existence of an electron-donating alkoxyalkyl group as a hemilabile arm slightly increases the electron density on the β-oxoiminato ligand. Complex **2a** showed the highest catalytic activity under the same conditions.

To further extend the scope of our Pd-catalytic system, we next investigated the combinatorial coupling of aryl halides with phenylboronic acid in the presence of **2a**. As shown in Table 2, various aryl iodides, bromides, and chlorides were subjected to the coupling reaction in aqueous DMA. High catalytic activity was observed in the coupling of activated 1-iodo-4-nitrobenzene and 1-iodo-3-nitrobenzene (Entries 1 and 2), as well as with deactivated aryl iodides such as 2-iodoanisole, 4-iodoanisole, 2-iodotoluene, and 4-iodophenol (Entries 3–6). Moreover, the catalyst showed outstanding activity in the coupling of substituted bromobenzenes with phenylboronic acid (Entries 7–12). Regardless of the substituents, all of the aryl bromides were consumed completely in short reaction times. A catalyst loading of 0.01 mol-% was sufficient to achieve high TOFs. Deactivated aryl bromides possessing electron-donating

Table 2. Suzuki–Miyaura coupling of aryl halides with phenylboronic acid.[a]



Entry	Substrate	T [°]	**2a** [mol-%]	Time [h]	Yield [%][b]
1		65	0.01	0.5	100 (95)
2		65	0.01	0.5	100
3		65	0.01	1	94
4		65	0.01	0.8	96 (91)
5		65	0.01	1	93
6		65	0.01	0.7	98
7		65	0.01	1.2	97 (92)
8		40	0.01	2.5	96
9		65	0.001	3	91
10		65	0.01	0.8	99
11		65	0.01	1.5	95
12		65	0.01	1.5	97
13		65	0.1	6	95 (91)
14		40	0.1	36	90
15		65	0.01	18	90
16		65	0.1	6	99
17		65	0.1	8	87
18		90	0.1	6	89 (81)
19		90	0.01	18	74
20		90	0.1	6	93
21		90	0.01	18	79 (70)

[a] Reactions were performed with a molar ratio of aryl iodide/phenylboronic acid/base = 1.0:1.1:2.0 in 50% aqueous DMA. [b] The yield was determined by GC using *n*-dodecane as the internal standard and based on the amount of arylbenzene employed. The isolated yield is given in parentheses.

groups showed a slight drop in reactivity relative to those with electron-withdrawing groups. However, high yields were still obtained at 65 °C in less than 1.5 h.

Encouraged by these results, we undertook the coupling of several aryl chlorides (Entries 13–21). It is well known that C–Cl activation is much more difficult than C–Br and C–I activation. Surprisingly, the coupling of chlorobenzene at 65 °C in the presence of 0.1 mol-% of **2a** proceeded with 95% yield in 6 h. When the reaction temperature was lowered to 40 °C, the reaction proceeded readily to afford 90% yield after 36 h under identical conditions. By decreasing the catalyst loading to 0.01 mol-%, 90% yield was obtained in 18 h. Activated 1-chloro-4-nitrobenzene was coupled almost quantitatively at 65 °C in 6 h (Entry 16). A temperature of 90 °C was required to reach satisfactory conversions. An attempt to couple deactivated aryl chloride was also successful to some extent. The coupling reactions of 4-chlorotoluene and 4-chloroanisole with phenylboronic acid proceeded smoothly to afford the corresponding coupling products in high yields.

Conclusions

We have demonstrated that (β-oxoiminato)palladium complexes can be used as highly efficient catalysts in Suzuki–Miyaura coupling reactions in aqueous media. Various aryl iodides and bromides were coupled with phenylboronic acid in short times and at mild temperatures. The catalyst system was also effective in the reactions of aryl chlorides. Further studies of other coupling reactions catalyzed by this system are currently in progress.

Experimental Section

General Remarks: Reagents were used as received from commercial sources. All manipulations were conducted under dry nitrogen. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Varian Unity Inova 400 NMR spectrometer at 400, 100, and 162 MHz, respectively. ^{31}P NMR chemical shifts were referenced to external PPh_3 in $CDCl_3$ at δ = 0 ppm. Elemental analyses were performed with an EA-1110 apparatus (CE Instruments). The diffraction data for a single crystal of **2a** were collected with a Bruker CCD diffractometer with Mo-K_α (λ = 0.71073) radiation by employing a 2 kW sealed tube X-ray source operating at 1.6 kW. The reflections were successfully indexed by using an automated indexing routine built into the SMART program.[14a] The CCD data were integrated and scaled using the Bruker SAINT program,[14b] and the structure was solved and refined by using XPREP[15a] and SHELX-97.[15b] CCDC-608595 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Synthesis of β-Oxoimines: 2-Methoxybenzylamine (1.64 g, 12.0 mmol) was added to a solution of 2,4-pentanedione (1.0 g, 10.0 mmol) in EtOH (20 mL). After refluxing for 24 h, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate, 4:1) to give β-oxoimine **1a** as a light yellow liquid (1.98 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.11 (br. s, 1 H), 7.23 (t, J = 8.0 Hz, 1 H), 7.17 (d, J = 8.0 Hz, 1 H), 6.91 (t, J = 7.6 Hz, 1 H), 6.85 (d, J = 8.4 Hz, 1 H), 4.99 (s, 1 H), 4.41 (d, J = 6.8 Hz, 1 H), 3.84 (s, 3 H), 2.00 (s, 3 H), 1.92 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.4, 162.7, 156.6, 128.4, 127.5, 126.0, 120.3, 110.0, 95.3, 55.1, 42.1, 28.7, 18.6 ppm. $C_{13}H_{17}NO_2$ (219.28): calcd. C 71.21, H 7.81, N 6.39; found C 71.02, H 7.54, N 6.58.

1b: Yield: 98% (1.68 g) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.73 (br. s), 4.83 (s, 1 H), 3.31 (t, J = 6.0 Hz, 2 H), 3.28 (s, 3 H), 3.22 (q, J = 3.6 Hz, 2 H), 1.86 (s, 3 H), 1.80 (s, 3 H), 1.67 (m, J = 2.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 162.4, 94.5, 68.7, 56.0, 39.3, 29.7, 28.1, 18.1 ppm. $C_9H_{17}NO_2$ (171.24): calcd. C 63.13, H 10.01, N 8.18; found C 63.41, H 10.18, N 8.21.

1c: Yield: 95% (1.34 g) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.94 (br. s, 1 H), 4.94 (s, 1 H), 3.20 (q, J = 3.6 Hz, 2 H), 1.97 (s, 3 H), 1.91 (s, 3 H), 1.61 (q, J = 3.6 Hz, 2 H), 0.98 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 162.2, 94.2, 44.0, 28.0, 22.8, 18.1, 10.7 ppm. $C_8H_{15}NO$ (141.21): calcd. C 68.04, H 10.71, N 9.02; found C 68.17, H 10.79, N 9.32.

1d: Yield: 80% (1.24 g) as a brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.24 (br. s, 1 H), 4.87 (s, 1 H), 2.03 (s, 3 H), 1.95 (s, 3 H), 1.37 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 163.0, 96.1, 52.2, 30.74, 28.7, 20.4 ppm. $C_9H_{17}NO$ (155.24): calcd. C 69.63, H 11.04, N 9.02; found C 69.54, H 11.38, N 9.13.

General Procedure for the Synthesis of (β-Oxoiminato)palladium Complexes: A solution of $Tl(OC_2H_5)$ (0.3 g, 1.2 mmol) in THF (10 mL) was added dropwise at room temperature to a solution of β-oxoimine **1a** (0.22 g, 1.0 mmol) in THF (10 mL). After stirring at room temperature for 1 h, a solution of $[Pd_2(PPh_3)_2Me_2(\mu\text{-}Cl)_2]$ (0.51 g, 0.6 mmol) in THF (5 mL) was added dropwise to the mixture. The reaction mixture was stirred at room temperature for 1 h and then filtered through Celite on a frit. The solvent was removed under reduced pressure, and the residue was washed with hexane (30 mL) and extracted with dichloromethane (10 mL). Removal of the solvent gave the Pd complex **2a** as a light brown solid (0.45 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.17 (m, 17 H), 6.92 (t, J = 4.0 Hz, 1 H), 6.81 (d, J = 4.4 Hz, 1 H), 4.83 (s, 1 H), 4.72 (d, J = 3.6 Hz, 2 H), 3.81 (s, 3 H), 1.89 (s, 3 H), 1.61 (s, 3 H), –0.08 (d, J = 3.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.0, 166.7, 156.0, 134.9, 134.8, 131.4, 131.0, 130.0, 129.9, 127.8, 127.7, 127.1, 126.6, 120.3, 109.2, 97.6, 55.2, 49.0, 26.4, 23.3, 23.2, –0.8 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 44.31 ppm. $C_{32}H_{34}NO_2PPd$ (602.01): calcd. C 63.84, H 5.69, N 2.33; found C 63.74, H 5.53, N 2.10.

2b: Yield: 70% (0.39 g) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.28 (m, 15 H), 4.72 (s, 1 H), 3.61 (m, 2 H), 3.44 (t, J = 6.2 Hz, 2 H), 3.41 (s, 3 H), 2.02 (s, 3 H), 1.92 (m, 2 H), 1.55 (s, 3 H), 0.11 (d, J = 3.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7, 141.9, 129.0–126.4 (PPh_3, 18 C), 95.33, 63.8, 51.8, 50.2, 30.7, 26.4, 24.8, 11.9 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 43.76 ppm. $C_{28}H_{34}NO_2PPd$ (553.97): calcd. C 60.71, H 6.19, N 2.53; found C 61.12, H 6.00, N 2.25.

2c: Yield: 71% (0.37 g) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.25 (m, 15 H), 4.69 (s, 1 H), 3.44 (m, 2 H), 1.99 (s, 3 H), 1.62 (m, 2 H), 1.52 (s, 3 H), 0.91 (t, J = 7.2 Hz, 3 H), 0.09 (d, J = 3.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.8, 163.9, 134.8–127.7 (PPh_3, 18 C), 97.7, 52.1, 26.2, 25.7, 23.5, 22.6, 11.5, 11.5, –1.8 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 43.75 ppm. $C_{27}H_{32}NOPPd$ (523.94): calcd. C 61.89, H 6.16, N 2.67; found C 61.66, H 5.71, N 3.06.

2d: Yield: 76% (0.41 g) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.37 (m, 15 H), 5.27 (s, 1 H), 2.01 (s, 3 H), 1.71 (s, 3 H), 1.15 (s, 9 H) 0.55 (t, J = 2.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 157.7, 152.1, 151.4, 150.6, 135.6, 132.5, 131.4, 127.5, 127.4, 123.6, 123.5, 123.0, 93.5, 50.1, 30.0, 24.8, 23.4, 19.2, 18.9, 0.8 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 44.11 ppm. $C_{28}H_{34}NOPPd$ (537.97): calcd. C 62.51, H 6.37, N 2.60; found C 62.40, H 5.78, N 3.10.

General Procedure for the Suzuki–Miyaura Reaction: Reactions were carried out in a glass ampoule equipped with a Teflon screw cap. Aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol), Na_2CO_3 (2.0 mmol), and *n*-dodecane (15–20 mg) as an internal GC standard were dissolved in DMA/H_2O (3 mL, 1:1), and then a solution of the given amount of catalyst **2a** in DMA (1.0 μmol mL^{-1}) was added to the mixture. The resulting mixture was stirred at the appropriate temperature (see Tables 1 and 2). Samples were withdrawn periodically and analyzed by GC/GC-MS. GC yields are based on the amount of aryl halide employed. The reaction mixture was filtered and washed with H_2O and Et_2O several times. The organic phase was separated and dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The product was isolated by column chromatography on silica gel.

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