

Bis(imino)pyridine palladium(II) complexes as efficient catalysts for the Suzuki–Miyaura reaction in water

Ping Liu*, Mei Yan and Ren He



Bis(imino)pyridine palladium(II) complexes **3** and **4** of type $[\text{PdCl}(\text{L})\text{PF}_6]$ are found to be efficient catalysts for Suzuki–Miyaura reactions of aryl halides and arylboronic acids. The reactions proceed smoothly to generate the corresponding biaryl compounds in moderate to excellent yields. The synthesis of various fluorinated biphenyl derivatives was successfully achieved by the complex **4** catalyzed the Suzuki–Miyaura reaction in the presence of surfactants bearing a long alkyl chain. Copyright © 2009 John Wiley & Sons, Ltd.

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Keywords: bis(imino)pyridine; palladium(II); Suzuki–Miyaura reaction; water; liquid crystalline compounds

Introduction

The synthesis of biaryl units in many kinds of compounds,^[1,2] including pharmaceuticals, herbicides and natural products, as well as in the field of engineering materials, such as conducting polymers, molecular wires and liquid crystals, has attracted enormous interest from the chemistry community. The palladium-catalyzed Suzuki–Miyaura reaction is the most important and efficient strategy for the construction of unsymmetrical biaryl compounds.^[3–6] Phosphine-based ligands remain by far the most popular selection in this reaction.^[7–13] However, most of the phosphine ligands are air- and moisture-sensitive, and P–C bond degradation sometimes occurs at elevated temperatures, which leads to palladium aggregation and eventually affects the overall catalytic performance.^[14] Therefore, recently the application of nitrogen-based ligands in the Pd-catalyzed Suzuki–Miyaura reaction has opened up new opportunities, such as Schiff bases,^[15–21] aryloximes,^[22,23] arylimines,^[24–28] *N*-acylamidines,^[29] guanidine,^[30] bis(oxazolonyl)pyrrole^[31] and simple amines.^[32–37] Bis(imino)pyridine as tridentate ligands have received considerable attention over the past decade, mainly due to the discovery of the high catalytic activity of their Fe and Co complexes in olefin polymerization.^[38–41] To the best of our knowledge, few investigations have been carried out on the synthesis and catalytic activity of bis(imino)pyridine palladium(II) complexes.^[42] In our previous work, bis(imino)pyridine palladium(II) complexes of types $[\text{PdCl}(\text{L})]_2\text{PdCl}_4$ and $[\text{PdCl}(\text{L})]\text{PdCl}_3$ have been used successfully to catalyze the Suzuki–Miyaura reaction in water.^[43,44] In this paper, we report the synthesis of new bis(imino)pyridine palladium(II) complexes $[\text{PdCl}(\text{L})\text{PF}_6]$, and their structure and catalytic activity for the Suzuki–Miyaura reaction in water.

Experimental

Materials and Methods

Infrared spectra were obtained as KBr pellets on a Perkin–Elmer FT–IR 430 spectrometer. ¹H NMR spectral data were recorded on a

Bruker DPX-400 spectrometer using TMS as internal standard and CDCl_3 as solvent. EI–mass spectra were measured on a LC/Q–TOF MS (Micromass, UK). Dichloromethane was dried over CaH_2 , distilled and stored under nitrogen. All other reagents were of analytical grade and used as received unless noted otherwise.

Synthesis of Complexes **3** and **4**

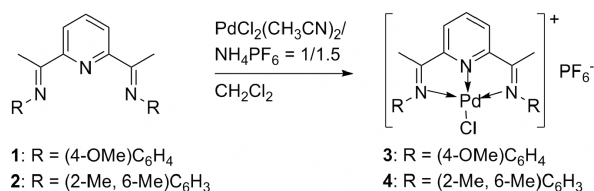
0.20 mmol of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ and 0.30 mmol of NH_4PF_6 were dissolved in 10 ml of CH_2Cl_2 . The solution was stirred at room temperature for 12 h followed by the addition of 0.20 mmol of ligand. After 24 h, the reaction mixture was filtered, and ether (100 ml) was added into the filtrate and a yellow solid was formed. The yellow precipitate was filtered, washed with ether (2×10 ml) and dried *in vacuo* to afford **3** or **4** as a yellow powder.

3: Yield 74%. Anal. calcd for $\text{C}_{23}\text{H}_{23}\text{ClF}_6\text{N}_3\text{O}_2\text{PPd}$: C, 41.84; H, 3.51; N, 6.36; found: C, 41.37; H, 3.68; N, 6.35. ¹H NMR (400 MHz, CDCl_3): δ 8.46 (t, $J = 8.4$ Hz, 1H, Py–Hp), 8.11 (d, $J = 8.4$ Hz, 2H, Py–Hm), 7.07 (d, $J = 9.2$ Hz, 4H, Ar–H), 6.88 (d, $J = 9.2$ Hz, 4H, Ar–H), 3.78 (s, 6H, OMe), 2.43 (s, 6H, N=CMe). ¹³C NMR (100 MHz, d_6 -DMSO): δ 19.06 (C5 and C5'), 55.35 (C10 and C10'), 113.66 (C8 and C8'), 124.47 (C7 and C7'), 129.25 (C2 and C2'), 137.79 (C1), 142.77 (C6 and C6'), 155.22 (C3 and C3'), 158.60 (C9 and C9'), 183.40 (C4 and C4'). IR (KBr, cm^{-1}): 1635 (C=N). HRMS (EI), m/z : $[\text{M} - \text{PF}_6]^+$, calculated for: 514.0514; found, 513.8875. m/z : $[\text{PF}_6]^-$ calculated for: 144.9642; found, 145.0418.

4: Yield 75%. Anal. calcd for $\text{C}_{25}\text{H}_{27}\text{ClF}_6\text{N}_3\text{PPd} \cdot 0.25\text{CH}_2\text{Cl}_2$: C, 44.76; H, 4.09; N, 6.20; found: C, 45.40; H, 4.22; N, 6.37. ¹H NMR (400 MHz, CDCl_3): δ 8.71 (t, $J = 8.0$ Hz, 1H, Py–Hp), 8.50 (d, $J = 8.0$ Hz, 2H, Py–Ho), 7.17–7.12 (m, 6H, Ar–H), 2.39 (s, 6H, N=CMe), 2.60 (s, 12H, CMe). ¹³C NMR (100 MHz, d_6 -DMSO): δ

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Scheme 1. Synthesis of bis(imino)pyridine palladium(II) complexes **3** and **4**.

17.62 (C5 and C5'), 17.94 (C10 and C10'), 127.75 (C2 and C2'), 128.07 (C9 and C9'), 129.26 (C7 and C7'), 130.26 (C8 and C8'), 142.56 (C1), 142.71 (C6 and C6'), 154.33 (C3 and C3'), 185.10 (C4 and C4'). IR (KBr, cm⁻¹): 1632 (C=N). HRMS (EI), *m/z*: [M – PF₆]⁺ calculated for: 510.0928; found: 509.9795; *m/z*: [PF₆]⁻ calculated for: 144.9642; found: 144.7618.

General Procedure for the Suzuki–Miyaura Reaction

A mixture of aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), K₃PO₄·3H₂O (1.20 mmol) and complex **4** (0.50 mol%) in 2 ml of water was heated to 80 °C and stirred under an air atmosphere for 1–3 h. When the reaction was completed, the mixture was cooled to room temperature and extracted with ether (5 × 2 ml). The combined extracts were dried over sodium sulfate, and concentrated under vacuum. The residue was purified using a silica gel column (petroleum as eluent) to give products.

X-ray Crystallography

Single crystal of complex **4** was obtained by slow diffusion of hexane into saturated dichloromethane solution. Suitable crystal for X-ray diffraction was mounted on a glass fiber. Data collection was performed on a Bruker Smart Apex CCD diffractometer using graphite monochromated Mo K_α radiation (λ = 0.71073 Å) at 273 K. The diffraction frames were integrated using the SAINT package. The structure was solved by direct methods using the program SHELXS97. Structure refinement by the full-matrix least-squares on *F*² was carried out with the program SHELXL97. All non-hydrogen atoms of the complex were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the Uiso values of their respective parent atoms.

Result and Discussion

First, bis(imino)pyridine ligands **1** and **2** were synthesized according to literature methods.^[45] Bis(imino)pyridine palladium(II) complexes **3** and **4** of type [PdCl(L)PF₆] were prepared by reaction of the mixture of PdCl₂(CH₃CN)₂ and 1.5 equiv. of NH₄PF₆ with 1.0 equiv. of bis(imino)pyridine ligands in CH₂Cl₂ for 24 h at room temperature (Scheme 1). Their structures contained one [PdCl]⁺ and one PF₆⁻ were initially confirmed by ¹H NMR spectroscopy, elemental analysis and HRMS(EI). The crystallographic analysis of complex **4** revealed the expected Pd(II) distorted square planar geometry with ligand **2**. The proposed coordination pattern is different from the bis(imino)pyridine palladium complexes that have been reported.^[46–49] The crystal structure plot is shown in Fig. 1. The important bond lengths and angles are summarized in Table 1.

Next, the catalytic activity of complexes **3** and **4** in the Suzuki–Miyaura reaction of 4-bromoanisole with phenylboronic

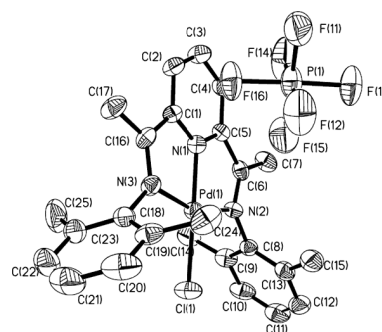


Figure 1. Structure of complex **4** at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (deg) for complex **4**

Bond lengths		Bond angles	
Pd(1)–N(1)	1.923(5)	N(1)–Pd(1)–N(2)	80.0(2)
Pd(1)–N(2)	2.034(5)	N(1)–Pd(1)–N(3)	79.7(2)
Pd(1)–N(3)	2.039(5)	N(3)–Pd(1)–Cl(1)	98.60(17)
Pd(1)–Cl(1)	2.267(2)	N(2)–Pd(1)–Cl(1)	101.63(16)
P(1)–F(11)	1.544(7)	F(13)–P(1)–F(14)	90.7(3)

acid was investigated with K₃PO₄·3H₂O as base at 80 °C. Initially, the model reaction proceeded smoothly in toluene to afford the corresponding product **7a** in 90% yield (Table 2, entry 1). Further investigation revealed that the result could be improved when water was used as solvent in the reaction (93 and 94%, Table 2, entries 2 and 3). With complex **4** as the catalyst, a number of aryl bromides and arylboronic acid were examined and the results are summarized in Table 2. The electron-poor 4-bromoacetophenone reacted with different arylboronic acids to give excellent yields after 3 h of reaction at 80 °C (96–98%, entries 4, 11, 15). The electron-rich 4-bromoanisole reacted with phenylboronic to also give good yield after 5 h of reaction (85%, entry 5). Aryl bromides containing an *ortho*-substituent also reacted effectively to furnish the desired biaryl products in good yields (80%, entry 6). It is noteworthy that the coupling reactions of water-soluble aryl bromides, such as 4-bromophenol and 4-bromobenzoic acid, with arylboronic acids were completed rapidly in excellent yields for only 1 h (98 and 99%, respectively, entries 8 and 9). The cross-coupling reactions of various aryl chlorides and arylboronic acids have also been investigated in DMA (*N,N*-dimethylacetamide) at 100 °C. The coupling reactions of aryl chlorides bearing an electron-withdrawing group, such as 4-CN, 4-COCH₃ and 4-NO₂, with arylboronic acids gave biaryls in good yields ranging from 85 to 96% after 3 h of reaction (entries 16–18 and 20). However, the electron-rich 3-chloroanisole reacted with 4-methylphenylboronic to give only 25% yield (entry 21), whereas 4-chloroanisole gave no reaction under the same conditions (entry 19).

From the above results, we can conclude that the water-solubility of aryl bromides has an obvious effect on the Suzuki–Miyaura reaction in water. Therefore, when this catalytic system was used to synthesize fluorinated biphenyl liquid crystal compounds by the reaction of aryl bromide **6h** with 4-fluorophenylboronic acid **5b**, the coupling product **7n** was not obtained, probably because of the low solubility of aryl bromide **6h** with a long alkyl chain in water (Table 3, entry 1). So it is

Table 2. Suzuki–Miyaura reaction catalyzed by complex **4**^{a,b}

Entry	R ₁	R ₂ , X	Product	Time (h)	Yield (%) ^c
1 ^d	H (5a)	4-OMe, Br (6a)	7a	3	90
2 ^e	H (5a)	4-OMe, Br (6a)	7a	3	93
3	H (5a)	4-OMe, Br (6a)	7a	3	94
4	H (5a)	4-OMe, Br (6b)	7b	3	96
5	H (5a)	4-Me, Br (6c)	7c	5	85
6	H (5a)	2-Me, Br (6d)	7d	5	80
7	H (5a)	4-F, Br (6e)	7e	5	90
8	H (5a)	4-COOH, Br (6f)	3f	1	99
9	H (5a)	4-OH, Br (6g)	7g	1	98
10	4-F (5b)	4-OMe, Br (6a)	7h	3	91
11	4-F (5b)	4-OMe, Br (6b)	7i	3	96
12	4-F (5b)	4-COOH, Br (6f)	7g	1	97
13	4-F (5b)	4-OH, Br (6g)	7k	1	98
14	4-Me (5c)	4-OMe, Br (6a)	7l	3	94
15	4-Me (5c)	4-OMe, Br (6b)	7m	3	98
16	H (5a)	4-NO ₂ , Cl (6h)	7n	3	96
17	H (5a)	4-CN, Cl (6i)	7o	3	93
18	H (5a)	4-OMe, Cl (6j)	7i	3	88
19	H (5a)	4-OMe, Cl (6k)	7a	3	0
20	4-Me (5c)	4-OMe, Cl (6j)	7i	3	85
21	4-Me (5c)	3-OMe, Cl (6l)	7j	3	25

^a Reaction conditions: aryl bromide 0.50 mmol, arylboronic acid 0.75 mmol, K₃PO₄·3H₂O 1.20 mmol, **4** (0.50 mol%), H₂O 2.0 ml, 80 °C.
^b Reaction conditions: aryl chloride 0.25 mmol, arylboronic acid 0.40 mmol, K₃PO₄·3H₂O 0.50 mmol, **4** (0.25 mol%), DMA 2.0 ml, 100 °C.
^c Isolated yields.
^d Toluene as solvent, complex **4** (0.50 mol%) as precatalyst.
^e Complex **3** (0.50 mol%) as precatalyst.

Table 3. Effect of surfactant on the Suzuki–Miyaura reaction^a

Entry	Surfactant (mol%)	Yield (%) ^b
1	–	0
2	TBAB (25)	0
3	TBAI (25)	0
4	CTAB (25)	95
5	CTAB (5.0)	94
6	CTAB (2.5)	93
7	SDBS (2.5)	92
8	Sodium dodecane-1-sulfonate (2.5)	90
9	1-Hexadecylpyridinium chloride (2.5)	91

^a Reaction conditions: aryl bromide 0.50 mmol, arylboronic acid 0.75 mmol, K₃PO₄·7H₂O 1.20 mmol, **4** (0.5 mol%), H₂O 2.0 ml, 80 °C, 3 h.
^b Isolated yields.

necessary to add a suitable surfactant in this system. Next, we explored the effect of a variety of surfactants on the coupling reaction (Table 3). The experiment result shows that the surfactants with short alkyl chains are ineffective, such

as TBAB and TBAI (entries 1 and 2). By contrast, when we performed the reaction using different concentrations of CTAB (hexadecyltrimethylammonium bromide) as the surfactant, good yields were obtained (93–95%, entries 4–6). Other surfactants

Table 4. Synthesis of TFT-LCDs by complex **4** catalyzed Suzuki–Miyaura reaction^a

Entry	R ₁	R ₂	Product	Yield (%) ^b
1	5b	4,4'-Propyl-cyclohexyl (6i)	7o	95 ^c /96 ^d
2	5b	4,4'-Pentyl-bicyclohexyl (6j)	7p	81 ^c /80 ^d
3	3,4-Difluoro (5d)	6h	7q	91 ^c /89 ^d
4	3,4,5-Trifluoro (5e)	6h	7r	90 ^c /90 ^d

^a Reaction conditions: aryl bromide 0.50 mmol, arylboronic acid 0.75 mmol, K₃PO₄·3H₂O 1.20 mmol, **4** (0.50 mol%), H₂O 2.0 ml, 80 °C, 3 h.

^b Isolated yields.

^c CTAB (2.5 mol%).

^d SDBS (2.5 mol%).

with long alkyl chains were also effective (90–92%, entries 7–9), irrespective of the hydrophilic head group (cationic or anionic). In fact, this is an important precondition for the formation of micelles that the surfactants possess a long alkyl chain and the hydrophobic chain must have a certain length (>C₁₀) to enable successful micelle formation.^[50]

This new protocol was also applied to the synthesis of other liquid crystal compounds, with CTAB and SDBS (sodium 4-dodecylbenzenesulfonate) as surfactants. The products **7o–7r** could be obtained in good yields (80–96%) for 3 h (Table 4). Thus, this method provides an efficient way to prepare biphenyl derivatives used as liquid crystal compounds.

Conclusion

In conclusion, we have synthesized air- and moisture-stable bis(imino)pyridine palladium(II) complexes **3** and **4** and investigated their catalytic activity for the Suzuki–Miyaura reaction in water. The synthesis of various fluorinated biphenyl derivatives was successfully achieved using complex **4** in the presence of surfactants bearing a long alkyl chain. This approach develops a green chemistry process and provides a practical procedure for the synthesis of fluorinated liquid crystals in industrial application.

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Supporting information

Supporting information may be found in the online version of this article.

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