Full Paper

Applied Organometallic Chemistry

Received: 22 August 2008 Revised: 8 December 2008 Accepted: 8 December 2008 Published online in Wiley Interscience

(www.interscience.com) DOI 10.1002/aoc.1481

Preparation and catalytic properties of bis(imino)pyridine palladium(II) complexes as efficient catalysts for Suzuki cross-coupling reaction in water

Ping Liu, Wenzhen Zhang and Ren He*

Air-stable bis(imino)pyridine palladium(II) complexes were synthesized and complex 12 proved to be a highly efficient catalyst for the Suzuki cross-coupling reaction between aryl bromides and arylboronic acids in air using water as solvent. The coupling reaction proceeded smoothly under mild conditions to provide biaryls in excellent yields and Pd black was not observed. The recycling of the catalysts was also investigated, for up to three cycles, and complex 12 still exhibited good activity.

Keywords: bis(imino)pyridine; Suzuki cross-coupling reaction; water

Introduction

Palladium-catalyzed Suzuki cross-coupling reaction has become one of the most powerful tools for the formation of C–C bonds in organic synthesis.[1–7] For many years, phosphines have been the most commonly employed ligands for the reaction. However, these types of ligands are generally either air/moisture-sensitive or expensive, and easily form Pd black, which places significant limits on their synthetic applications. Hence, the development of phosphine-free *N*-based ligands is of current interest. *N*-heterocyclic carbenes,[8–21] *N*,*O*- or *N*,*N*-bidentate ligands,[22–29] aryloximes,[30,31] arylimines,[32–36] *N*-acylamidines,[37] guanidine[38] and simple amines[39–44] have been used in the Suzuki cross-coupling reaction. and water has attracted attention as a potential replacement for organic solvents because of its low cost, nonflammability and low toxicity in the Suzuki coupling reaction. Although a palladium-catalyzed Suzuki coupling reaction in water has been developed, most of these systems require phase-transfer catalysts.[45–52] In addition, the liquid crystalline materials containing monofluoro-, difluoro- or trifluoro-substituted phenyls[53–56] are the most interesting for application in thin-film transistor liquid crystal displays. The long, lath-like molecular structure of most fluorinated liquid crystalline compounds demanded by thin-film transistor liquid crystal displays makes cross-coupling reactions very important in synthesis.

In this paper, we describe palladium-catalyzed Suzuki coupling reactions in water using air-stable bis(imino)pyridine as ligands and wish to report a general and efficient method for the synthesis of fluorinated liquid crystalline compounds via Suzuki cross-coupling reactions.

Experimental

Materials and Instruments

Infrared spectra were obtained as KBr pellets on a Perkin–Elmer FT-IR 430 spectrometer. ^{1}H NMR and ^{13}C NMR spectral data were recorded on Bruker DPX-400 spectrometers using TMS as internal standard and $CDCl_3$ or d_6-DMSO as solvent. Elemental analyses (C, H, N) were conducted with a Vario EL III elemental analyzer. Cl was analyzed by oxygen flask combustion. EI-mass spectra were measured on an LC/Q-TOF MS (Micromass, UK). Acetonitrile was dried over CaH_2, distilled and stored under nitrogen. Methanol was dried and distilled from Mg. All other reagents were of analytical-grade quality purchased commercially and used as received unless noted otherwise.

Synthesis of ligands 1–6

Bis(imino)pyridine **1–6** were synthesized according to literature methods.[57]

1

White solid, yield 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, J = 8.0 Hz, 2H, Py–Hm), 7.60 (t, J = 8.0 Hz, 1H, Py–Hp), 5.50 (s, 4H, N–H), 2.30 (s, 6H, N=CMe). IR (KBr, cm^{-1}): 1640 (C= N).

2

Yellow solid, yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.07 (d, J = 8.0 Hz, 2H, Py–Hm), 7.67 (t, J = 8.0 Hz, 1H, Py–Hp), 7.53 (s, 2H, N–H), 7.30 (t, J_1 = 8.4 Hz, J_2 = 7.6 Hz, 4H, Ar–H), 7.20 (d, J = 7.6 Hz, 4H, Ar–H), 6.91 (t, J = 8.4 Hz, 2H, Ar–H), 2.44 (s, 6H, N=CMe). IR (KBr, cm^{-1}): 1692 (C= N).

* *Correspondence to: Ren He, State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, People's Republic of China. E-mail: heren@chem.dult.edu.cn*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, People's Republic of China

3

Yellow solid, yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.23 (d, J = 7.6 Hz, 2H, Py–Hm), 7.45 (t, J = 7.6 Hz, 1H, Py–Hp), 7.46–7.27 (m, 10H, Ar–H), 4.80 (s, 4H, CH_2), 2.54 (s, 6H, N=CMe). IR (KBr, cm^{-1}): 1631 (C= N).

4

Yellow solid, yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.41 (d, J = 8.0 Hz, 2H, Py–Hm), 7.89 (t, J = 8.0 Hz, 1H, Py–Hp), 7.25–7.19 (m, 4H, Ar–H), 7.04 (t, J = 7.6 Hz, 2H, Ar–H), 6.90 (d, J = 7.6 Hz, 2H, Ar–H), 2.35 (s, 6H, N=CMe), 2.13 (s, 6H, Ar–Me). IR (KBr, cm^{-1}): 1646 (C= N).

5

Yellow solid, yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.33 (d, J = 7.6 Hz, 2H, Py–Hm), 7.86 (t, J = 7.6 Hz, 1H, Py–Hp), 6.96–6.82 (m, 8H, Ar–H), 3.84 (s, 6H, N=CMe), 2.44 (s, 6H, OMe). IR (KBr, cm^{-1}): 1627 (C= N).

6

Yellow solid, yield 85%. ^{1}H NMR (400 MHz, $CDC1_3$) δ (ppm): 8.49 (d, J = 8.0 Hz, 2H, Py–Hm), 7.92 (t, J = 8.0 Hz, 1H, Py–Hp), 7.09–6.95 (m, 6H, Ar–H), 2.24 (s, 6H, N=CMe), 2.06 (s, 12H, Ar–Me). IR (KBr, cm^{-1}): 1645 (C= N).

Synthesis of Complexes 7–12

A 0.20 mmol aliquot of $PdCl_2(CH_3CN)_2$ and 0.20 mmol of ligand were dissolved in 10 ml of acetonitrile. The solution was stirred at room temperature for 2 h. Ether (50 ml) was added to the reaction mixture, and this mixture was placed for an appropriate period of time, after which it was filtered and the solid was obtained.

7

Yellow solid, yield 90%. Anal. calcd for $C_{18}H_{26}Cl_4N_{10}Pd_2 \cdot 4H_2O$: C, 26.72; H, 4.24; N, 17.31; Cl, 17.53. Found: C, 27.00; H, 4.01; N, 17.71, Cl, 17.30. ^{1}H NMR (400 MHz, d_6-DMSO) δ (ppm): 8.21 (t, J = 8.0 Hz, 1H, Py–Hp), 7.68 (m, 6H, 2H–Py–Hm and 4H–NH_2), 2.26 (s, 6H, N=CMe). ^{13}C NMR(100 MHz, d_6-DMSO) δ (ppm): 13.23 (CH_3), 122.22 (C), 142.98 (C), 152.90 (C), 155.84 (C=N). IR (KBr, cm^{-1}): 1603 (C=N). HRMS (EI), m/z: $[(M - X)/2]^+$; calculated: 331.9894; found, 331.8961.

8

Red solid, yield 89%. Anal. calcd for $C_{42}H_{42}Cl_2N_{10}Pd_2 \cdot PdCl_4$: C, 41.39; H, 3.47; N, 11.49; Cl, 17.45. Found: C, 39.13; H, 3.28; N, 11.85; Cl, 17.20. ^{1}H NMR (400 MHz, d_6-DMSO) δ (ppm): 9.48 (s, 1H, Py–Hp), 7.94 (d, J = 7.6 Hz, 2H, Py–Hm), 7.73 (s, 2H, N–H), 7.25 (d, J = 8.0 Hz, 4H, Ar–H), 7.19 (t, J_1 = 7.2 Hz, J_2 = 8.0 Hz, 4H), 6.76 (t, J_1 = 6.4 Hz, J_2 = 6.8 Hz, 2H), 2.37 (s, 6H, N=CMe). ^{13}C NMR (100 MHz, d_6-DMSO) δ (ppm): 10.24 (CH_3), 112.48 (C), 116.87 (C), 127.69 (C), 128.54 (C), 140.07 (C), 143.44 (C), 153.72 (C), 155.44 (C=N). IR (KBr, cm^{-1}): 1598 (C=N). HRMS (EI), m/z: $[(M - X)/2]^+$; calculated: 484.0520; found, 483.9798.

9

Yellow solid, yield 90%. Anal. calcd for $C_{46}H_{46}Cl_2N_6Pd_2 \cdot PdCl_4 \cdot CH_3CN$: C, 45.90; H, 3.93; N, 7.81; Cl, 16.94. Found: C, 45.86; H, 3.92; N, 7.82; Cl, 17.00. ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.54 (t, J = 7.6 Hz, 1H, Py–Hp), 8.42 (d, J = 7.6 Hz, 2H, Py–Hm), 7.53–7.30 (m, 10H, Ar–H), 5.06 (s, 4H, CH_2), 2.62 (s, 6H, N=CMe). ^{13}C NMR(100 MHz, d_6-DMSO) δ (ppm): 17.45 (CH_3), 56.89 (CH_2), 127.70 (C), 127.89 (C), 128.62 (C), 128.97 (C), 135.11 (C), 142.57 (C), 155.43 (C), 184.55 (C=N). IR (KBr, cm^{-1}): 1636 (C=N); HRMS (EI); m/z: $[(M - X)/2]^+$, calculated: 482.0615; found, 481.9999.

10

Yellow solid, yield 86%. Anal. calcd for $C_{46}H_{46}Cl_2N_6Pd_2 \cdot PdCl_4$: C, 45.48; H, 3.82; N, 6.92; Cl, 17.51. Found: C, 44.81; H, 3.66; N, 7.03; Cl, 17.12. ^{1}H NMR (400 MHz, d_6-DMSO) δ (ppm): 8.68 (t, J = 8.4 Hz, 1H, Py–Hp), 8.50 (d, J = 8.4 Hz, 2H, Py–Hm), 7.27–7.08 (m, 8H, Ar–H), 2.39 (s, 6H, N=CMe), 2.35–2.28 (d, 6H, Ar–Me). ^{13}C NMR (100 MHz, d_6-DMSO) δ (ppm): 16.88 (CH_3), 16.99 (CH_3), 17.70 (CH_3), 120.45 (C), 125.35 (C), 126.88 (C), 128.67 (C), 128.69 (C), 129.11 (C), 129.49 (C), 141.75 (C), 142.83 (C), 142.88 (C), 153.73 (C), 153.76 (C), 183.32 (C=N), 183.44 (C=N). IR (KBr, cm^{-1}): 1625 (C=N); HRMS (EI); m/z: $[(M - X)/2]^+$, calculated: 482.0615; found, 482.0117.

11

Yellow solid, yield 88%. Anal. calcd for $C_{46}H_{46}Cl_2N_6O_4Pd_2 \cdot PdCl_4 \cdot CH_3CN \cdot 2H_2O$: C, 42.52; H, 3.94; N: 7.23; Cl, 15.69. Found: C, 42.46; H, 3.97; N, 7.28, Cl, 15.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.71 (t, J = 6.8 Hz, 1H, Py–Hp), 8.42 (d, J = 6.8 Hz, 2H, Py–Hm), 7.22–6.81 (m, 8H, Ar–H), 3.70 (s, 6H, N=CMe), 2.57 (s, 6H, OMe). ^{13}C NMR(100 MHz, d_6-DMSO) δ (ppm): 19.16 (CH_3), 55.38 (CH_3), 113.65 (C), 124.52 (C), 129.34 (C), 137.83 (C), 155.21 (C), 158.58 (C), 183.40 (C=N). IR (KBr, cm^{-1}): 1603 (C=N). HRMS (EI), m/z: $[(M - X)/2]^+$; calculated: 514.0514; found, 514.0362.

12

Yellow solid, yield 90%. Anal. calcd for $C_{50}H_{54}Cl_2N_6Pd_2 \cdot PdCl_4 \cdot H_2O$: C, 46.59; H, 4.38; N, 6.52; Cl, 16.50. Found: C, 46.95; H, 4.37; N, 6.52; Cl, 16.06. ^{1}H NMR (400 MHz, $CDC1_3$) δ (ppm): 9.08 (t, J = 7.6 Hz, 1H, Py–Hp), 8.97 (d, J = 7.6 Hz, 2H, Py–Hm), 7.18–7.08 (m, 6H, Ar–H), 2.55 (s, 6H, N=CMe), 2.32 (s, 12H, Ar–Me). ^{13}C NMR(100 MHz, d_6-DMSO) δ (ppm): 17.98 (CH_3), 18.06 (CH_3), 127.76 (C), 128.08 (C), 129.29 (C), 130.36 (C), 142.58 (C), 142.72 (C), 154.34 (C), 185.16 (C=N). IR (KBr, cm^{-1}): 1625 (C=N). HRMS (EI); m/z: $[(M - X)/2]^+$, calculated: 510.0928; found, 510.0817.

General Procedure for Suzuki Cross-coupling Reaction

A 5 ml flask was charged with **12** (0.0025 mmol), $K_3PO_4 \cdot 3H_2O$ (1.20 mmol) and arylboronic acid (0.75 mmol), water or ethanol (2 ml), and aryl bromide (0.5 mmol) was added. The reaction was stirred at 80 °C for the correct time. After the reaction was allowed to cool to room temperature, the resulting mixture was extracted with ether (5 × 2 ml). The combined ether extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude material was flash chromatographed on a short silica gel column (the products **3n–3s** of the water-soluble aryl bromides do not require to a silica gel column to seperate, only recrystallization with ethanol).

Results and Discussion

Preparations of Complexes 7–12

Bis(imino)pyridine palladium(II) complexes (**7–12**) were prepared by reaction of $PdCl_2(CH_3CN)_2$ with 1 equiv. of ligands in acetonitrile at room temperature for 2 h (Scheme 1). Their structures contained two $[PdLCl]^+$ and two Cl^- or one $[PdCl_4]^{2-}$ were confirmed by elemental analysis, ^1H NMR, HRMS(EI) and IR spectroscopies. The proposed coordination pattern was evidenced by ^1H NMR spectra of the ligands; for example, complex **12** exhibited downfield shifts of the proton signals relative to those for ligand **6**, and the change in the pyridine proton chemical shift values is obvious. For complex **12** and ligand **6**, the *para* protons of pyridine appear as a triplet at δ 9.08 and 7.92 ppm, respectively, and the meta protons of pyridine protons appear as a multiplet at δ 8.97 and 8.48 ppm. IR spectra of complex **12** show ν (C═N) around 1625 cm^{-1}, and ligand **6** shows ν (C═N) around 1645 cm^{-1}, which indicates that the three nitrogen atoms of bis(imino)pyridine ligand coordinate with Pd(II).

Catalytic Suzuki Cross-coupling Reactions

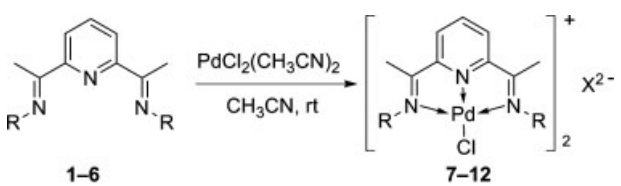
Bis(imino)pyridine palladium(II) complexes (**7–12**) were stable in air and diffluent in water. Therefore we carried out the Suzuki coupling reaction in air using water as solvent.

Effect of Catalyst on Suzuki Cross-coupling Reactions

To examine the efficiency of bis(imino)pyridine palladium(II) complexes in the Suzuki cross-coupling reaction, a model coupling reaction of 4-bromoanisole with phenylboronic acid was initially tested. The results are summarized in Table 1. These data show that these bis(imino)pyridines are effective ligands for the palladium-catalyzed Suzuki cross-coupling reaction. Among the bis(imino)pyridine palladium(II) complexes investigated, **7** and **8** showed moderate efficiency, which gave the coupling product in 70–76% yield (entries 1 and 2). Compounds **9–12** showed good efficiency (≥90%); **12** was found to be the best, and gave the coupling product in 95% yield (entry 6).

Effect of catalyst loading on Suzuki cross-coupling reactions

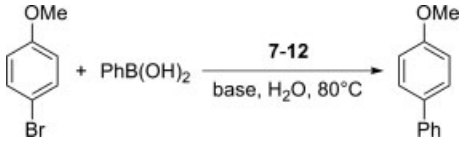
It is important to achieve good yields using minimum catalysts in mild reaction condition. We also examined the effect of catalyst loading on a convenient coupling between 4-bromoanisole and phenylboronic acid (Table 2). High yields (>90%) and a TON of 9000 were obtained even at catalyst loadings as low as 0.0025 mmol%. These are indications of an effective catalytic system that has commercial and industrial potential.



1, **7**: R = NH_2, X = Cl_2
2, **8**: R = NHPh, X = $PdCl_4$
3, **9**: R = CH_2Ph, X = $PdCl_4$
4, **10**: R = (2-Me)C_6H_4, X = $PdCl_4$
5, **11**: R = (4-OMe)C_6H_4, X = $PdCl_4$
6, **12**: R = (2-Me, 6-Me)C_6H_3, X = $PdCl_4$

Scheme 1. Synthesis of bis(imino)pyridine palladium(II) complexes **7–12**.

Table 1. Effect of **7–12** on Suzuki cross-coupling reactions[a]



Entry	Complexes	Yield (%)[b]
1	**7**	70
2	**8**	76
3	**9**	90
4	**10**	93
5	**11**	90
6	**12**	95

[a] Reaction conditions: 0.50 mmol 4-bromoanisole, 0.75 mmol phenylboronic acid, 1.2 mmol $K_3PO_4 \cdot 3H_2O$, **7–12** (0.25 mmol %), 2.0 ml H_2O, 80 °C, reaction time 3 h.
[b] Isolated yields.

Table 2. Effect of catalyst loading on Suzuki cross-coupling reactions[a]

12 (mmol %)	Yield (%)[b]	TON
0.25	98	98
0.025	96	960
0.0025	90	9000

[a] Reaction conditions: 0.50 mmol 4-bromoanisole, 0.75 mmol phenylboronic acid, 1.2 mmol $K_3PO_4 \cdot 3H_2O$, 2.0 ml H_2O, 80 °C, reaction time 4.5 h.
[b] Isolated yields.

Table 3. Effect of base on Suzuki cross-coupling reactions[a]

Entry	Base	Yield (%)[b]
1	NEt_3	0
2	KOAc	10
3	NaOAc	26
4	KOH	90
5	K_2CO_3	96
6	$K_3PO_4 \cdot 3H_2O$	99

[a] Reaction conditions: 0.50 mmol 4-bromoanisole, 0.75 mmol phenylboronic acid, 1.2 mmol base, **12** (0.25 mmol%), 2.0 ml H_2O, 80 °C, reaction time 5 h.
[b] Isolated yields.

Effect of Base on Suzuki Cross-coupling Reactions

The base usually plays an important role in Suzuki cross-coupling reaction. Thus, different kinds of bases were screened and the results are summarized in Table 3. $K_3PO_4 \cdot 3H_2O$, K_2CO_3 and KOH were better among these bases in the Suzuki cross-coupling reaction (Table 3, entries 4–6), and $K_3PO_4 \cdot 3H_2O$ was the best one (99%). When KOAc and NaOAc were used as bases (Table 3, entries 2 and 3), the yield of product was reduced to 10–26%. NEt_3 as an organic base was not efficient (Table 3, entry 1).

Suzuki Cross-coupling Reaction of Arylbromides and Boronic Acid

The cross-coupling reactions of various aryl bromides and arylboronic acids were investigated and representative results are given in Table 4. The electron-poor aryl bromides, such as 4-bromoacetophenone, reacted with different aryl boronic acids to give excellent yield at 80 °C for 3–10 h (Table 4, entries 2, 7 and 11). The electron-rich aryl bromide, such as 4-bromoanisole, also gave good yield at the same temperature for 4–10 h (Table 4, entries 1, 6 and 10). The aryl bromides containing *ortho* substituent also reacted effectively to prepare the desired sterically demanding biaryl products at the same condition in moderate to good yields (Table 4, entries 4 and 13). It is noteworthy that the water-soluble aryl bromides, such as 4-bromophenol and 4-bromobenzoic acid, gave good yields for only 1–2.5 h (Table 4, entries 15–20), and we found the products were easily separated from the reaction system by extaction. The products were then obtained easily by condensation and recrystallization.

In addition, we can use this new protocol to synthesize liquid crystal compounds, but considering the solubility of arylbromides, we select ethanol as the solvent. Rhe products **3t**–**3w** can be synthesized by this reaction to give excellent yields (≥90%) for 3 h (Table 4, entries 21–24). However, **3x** is obtained with only a 60% yield because the arylbromide is not soluble in ethanol at 80 °C.

Table 5. Recycling of **12**[a]

Cycles (*n*)/time (h)	0/5 h	1/5 h	2/10 h	3/10 h
Yield(%)[b]	98	96	93	94

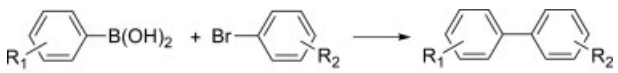
[a] Reaction conditions: 0.50 mmol 4-bromoanisole, 0.75 mmol phenylboronic acid, 1.2 mmol $K_3PO_4 \cdot 3H_2O$, **12** (0.25 mmol %), 2.0 ml H_2O, 80 °C.
[b] Isolated yields (average of two runs).

Thus, this method provides a highly efficient and mild method to prepare biphenyl derivatives used as liquid crystal compounds.

Recycling of Catalyst

Because the Pd black was not observed, the feasibility of recycling **12** was examined taking the coupling of phenylboronic acid with 4-bromoanisole as a model (Table 5, cycles 1–3). After the first cycle, extraction with ether allowed a separation of the coupling product from the water layer. The resulting aqueous phase was reused by the addition of the substrate and base. The reaction was repeated at 80 °C for the correct time, for up to three cycles; catalyst **12** still exhibited good activity.

Table 4. Suzuki cross-coupling reaction of arylbromides and boronic acid catalyzed by **12**[a]



1a-1e **2a-2j** **3a-3x**

Entry	R_1	R_2	Product	Time (H)	Yield (%)[b]
1	H (**1a**)	4-OMe (**2a**)	**3a**	5	99
2	**1a**	4-COMe (**2b**)	**3b**	3	99
3	**1a**	4-Me (**2c**)	**3c**	5	99
4	**1a**	2-Me (**2d**)	**3d**	5	83
5	**1a**	4-F (**2e**)	**3e**	5	95
6	4-F (**1b**)	**2a**	**3f**	10	91
7	**1b**	**2b**	**3g**	10	93
8	**1b**	**2c**	**3h**	10	85
9	**1b**	**2e**	**3i**	10	95
10	4-Me (**1c**)	**2a**	**3j**	4	96
11	**1c**	**2b**	**3k**	4	95
12	**1c**	**2c**	**3l**	4	98
13	**1c**	**2d**	**3m**	5	91
14	**1c**	**2e**	**3h**	4	97
15	**1a**	4-COOH (**2f**)	**3n**	2.5	92
16	**1a**	4-OH (**2g**)	**3o**	2	93
17	**1b**	**2f**	**3p**	2.5	91
18	**1b**	**2g**	**3q**	1	92
19	**1c**	**2f**	**3r**	2.5	90
20	**1c**	**2g**	**3s**	1	92
21	**1b**	4,4′-Propyl-cyclohexyl (**2h**)	**3t**	3	96
22	**1b**	4,4′-Pentyl-cyclohexyl (**2i**)	**3u**	3	90
23	3,4-Difluoro (**1d**)	**2i**	**3v**	3	91
24	3,4,5-Trifluoro (**1e**)	**2i**	**3w**	3	90
25	**1b**	4,4′-Pentyl-bicyclohexyl (**2j**)	**3x**	3	60

[a] Reaction conditions: 0.50 mmol aryl bromide, 0.75 mmol boronic acid, 1.2 mmol $K_3PO_4 \cdot 3H_2O$, **12** (0.25 mmol%), 2.0 ml H_2O or EtOH, 80 °C.
[b] Isolated yields.

Conclusion

In summary, complex **12** was found to be an excellent catalyst for Suzuki cross-coupling reactions of arylboronic acids and aryl bromides. These 3N ligands chelating Pd(II) complexes are air- and moisture-stable, and easy to prepare. A new catalytic system provides good conditions for the coupling of aryl bromides in high yields, and provides a practical procedure for the synthesis of fluorinated liquid crystals in industry applications.

Acknowledgments

We gratefully acknowledge financial support of this work by the National Natural Science Foundation of China (grant no. 20333060).

References

[1] N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, *11*, 513.
[2] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.
[3] A. Suzuki, In *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang). Wiley-VCH: Weinheim, **1998**, pp. 49–97.
[4] A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147.
[5] A. Suzuki, *J. Organomet. Chem.* **2002**, *83*, 653.
[6] Z.-S. Bo, A. D. Schlüter, *Chem. Eur. J.* **2000**, *6*, 3235.
[7] S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633.
[8] O. Navarro, N. Marion, Y. Oonishi, R. A. Kelly, S. P. Nolan, *J. Org. Chem.* **2006**, *71*, 685.
[9] A. I. Moncada, S. Manne, J. M. Tanski, L. M. Slaughter, *Organometallics* **2006**, *25*, 491.
[10] F.-L. Zeng, Z.-K. Yu, *J. Org. Chem.* **2006**, *71*, 5274.
[11] J.-W. Kim, J.-H. Kim, D.-H. Lee, Y.-S. Lee, *Tetrahedron Lett.* **2006**, *47*, 4745.
[12] T.-R. Kang, Q. Feng, M.-M. Luo, *Synlett* **2005**, 2305.
[13] M. Shi, H.-X. Qian, *Tetrahedron* **2005**, *61*, 4949.
[14] J. H. Kim, J. W. Kim, M. Shokouhimehr, Y. S. Lee, *J. Org. Chem.* **2005**, *70*, 6714.
[15] A.-E. Wang, J. Zhong, J.-H. Xie, K. Li, Q.-L. Zhou, *Adv. Synth. Catal.* **2004**, *346*, 595.
[16] G. Altenhoff, R. Goddard, C. W. Lehmann, F. Glorius, *Angew. Chem., Int. Ed.* **2003**, *42*, 3690.
[17] C. W. K. Gstôttmayr, V. P. W. Bôhm, E. Herdtweck, M. Grosche, W. A. Herrmann, *Angew. Chem., Int. Ed.* **2002**, *41*, 1363.
[18] W. A. Herrmann, *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.
[19] G. A. Grasa, M. S. Viciu, J. Huang, C. Zhang, M. L. Trudell, S. P. Nolan, *Organometallics* **2002**, *21*, 2866.
[20] C. Zhang, J. Huang, M. L. Trudell, S. P. Nolan, *J. Org. Chem.* **1999**, *64*, 3804.
[21] W. A. Herrmann, C.-P. Reisinger, M. Spiegler, *J. Organomet. Chem.* **1998**, *557*, 93.
[22] N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609.
[23] W.-Y. Wu, S.-N. Chen, F.-Y. Tsai, *Tetrahedron Lett.* **2006**, *47*, 9267.
[24] Y.-C. Lai, H.-Y. Chen, W.-C. Hung, C.-C. Lin, F.-E. Hong, *Tetrahedron* **2005**, *61*, 9484.
[25] D. Domin, D. Benito-Garagorri, K. Mereiter, J. Fróhlich, K. Kirchner, *Organometallics* **2005**, *24*, 3957.
[26] T. Mino, Y. Shirae, M. Sakamoto, T. Fujita, *J. Org. Chem.* **2005**, *70*, 2191.
[27] Z. Weng, S. Teo, L. L. Koh, T. S. A. Hor, *Organometallics* **2004**, *23*, 3603.
[28] C. Nájera, J. Gil-Molto, S. Karlstrom, L. R. Falvello, *Org. Lett.* **2003**, *5*, 1451.
[29] C. Mazet, L. H. Gade, *Organometallics* **2001**, *20*, 4144.
[30] L. Botella, C. Nájera, *Angew. Chem., Int. Ed.* **2002**, *41*, 179.
[31] D. A. Alonso, C. Nájera, M. C. Pacheco, *Org. Lett.* **2000**, *2*, 1823.
[32] Rongcai Huang, Kevin H. Shaughnessy, *Organometallics* **2006**, *25*, 4105.
[33] C. Rocaboy, J. A. Gladysz, *New J. Chem.* **2003**, *27*, 39.
[34] R. B. Bedford, C. S. J. Cazin, *Chem. Commun.* **2001**, 1540.
[35] R. B. Bedford, C. S. J. Cazin, M. B. Hursthouse, M. E. Light, K. J. Pike, S. Wimperis, *J. Organomet. Chem.* **2001**, *633*, 173.
[36] H. Weissman, D. Milstein, *Chem. Commun.* **1999**, 1901.
[37] J. K. Eberhardt, R. Fröhlich, E.-U. Würthwein, *J. Org. Chem.* **2003**, *68*, 6690.
[38] Shenghai Li, Yingjie Lin, Jungang Cao, and Suobo Zhang, *J. Org. Chem.* **2007**, *72*, 4067.
[39] J.-H. Li, X.-C. Hu, Y. Liang, Y.-X. Xie, *Tetrahedron* **2006**, *62*, 31.
[40] Jin-Heng Li, Xi-Chao Hu, Ye-Xiang Xie, *Tetrahedron. Lett.* **2006**, *47*, 9239.
[41] J.-H. Li, W.-J. Liu, Y.-X. Xie, *J. Org. Chem.* **2005**, *70*, 5409.
[42] J.-H. Li, W.-J. Liu, *Org. Lett.* **2004**, *6*, 2809.
[43] B. Tao, D. W. Boykin, *J. Org. Chem.* **2004**, *69*, 4330.
[44] B. Tao, D. W. Boykin, *Tetrahedron Lett.* **2003**, *44*, 7993.
[45] Wen-Jie Liu, Ye-Xiang Xie, Yun Liang, Jin-Heng Li, *Synthesis* **2006**, *5*, 860.
[46] Leifang Liu, Yuhong Zhang, and Yanguang Wang, *J. Org. Chem.* **2005**, *70*, 6122.
[47] Bhattacharya Santanu, Srivastava Aasheesh, Sengupta Saumitra, *Tetrahedron Lett.* **2005**, *46*, 3557.
[48] Calo Vincenzo, Nacci Angelo, Monopoli Antonio, Montingelli Floriana, *J. Org. Chem.* **2005**, *70*, 6040.
[49] Morin Deveau, Amy Macdonald, L Timothy, *Tetrahedron Lett.* **2004**, *45*, 803.
[50] Robin B. Bedford, Michael E. Blake, Craig P. Butts, Debbie Holder, *Chem. Commun.* **2003**, *4*, 466.
[51] D. Badone, M. Baroni, R. Cardamone, A. Ielmini, U. Guzzi, *J. Org. Chem.* **1997**, *62*, 7170.
[52] N. A. Bumagin, V. V. Bykov, I. P. Beletskaya, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1989**, *38*, 2206.
[53] Mengping Guo, Fangfang Jian, Ren He, *Journal of Fluorine Chemistry* **2006**, *127*, 177.
[54] M. Hird, G. W. Gray, K. J. Toynec, *Liq. Cryst.* **1992**, *4*, 531.
[55] M. F. Nabor, H. T. Nguyen, C. Destrade, J. P. Marcerou, *Liq. Cryst.* **1991**, *10*, 785.
[56] Y. Goto, K. Kitano, *European Patent* 387,032, **1991**.
[57] Rui-Qing Fan, Dong-Sheng Zhu, Ying Mu etc, *Eur. J. Inorg. Chem.* **2004**, 4891.

