



# [PdCl<sub>2</sub>{8-(di-*tert*-butylphosphinoxy)quinoline}]: a highly efficient catalyst for Suzuki–Miyaura reaction

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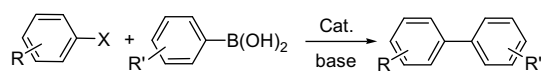
## ABSTRACT

The complex [PdCl<sub>2</sub>(P–N)] containing the basic and sterically demanding 8-(di-*tert*-butylphosphinoxy)quinoline ligand (P–N) is a highly efficient catalyst for the coupling of phenylboronic acid with aryl bromides or aryl chlorides. The influence of solvent and base has been investigated, the highest rates being observed at 110 °C in toluene with K<sub>2</sub>CO<sub>3</sub> as the base. With aryl bromides the reaction rates are almost independent on the electronic properties of the *para* aryl substituents, on the contrary, reduced reaction rates are observed when bulky substituents are present on the substrate. Nevertheless the coupling of 2-bromo-1,3,5-trimethylbenzene with phenylboronic acid can be carried out to completion in 2 h using a catalyst loading of 0.02 mol %. Under optimized reaction conditions, turnover frequencies as high as 1900 h<sup>-1</sup> can be obtained in the coupling of 4-chloroacetophenone with phenylboronic acid; lower reaction rates are obtained with substrates bearing EDG substituents on the aryl group.

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## 1. Introduction

The transition-metal-catalyzed coupling of aryl halides with arylboronic acids (Suzuki–Miyaura reaction, Scheme 1) has become a very important synthetic tool in organic chemistry and in particular it is largely employed for the synthesis of important intermediates such as biaryls.<sup>1</sup>



X = halogen, triflate

Scheme 1. Synthesis of biaryls via Suzuki–Miyaura reaction.

The larger and larger application of this coupling has been boosted by the availability of very efficient catalytic systems. Following the disclosure by Herrmann and Beller<sup>2</sup> that palladacycles are very efficient catalysts for the reaction, in the last decade catalytic systems able to give turnover numbers (TON) as high as 1,000,000 for the coupling of aryl bromides with aryl boronic acid have been reported by different groups.<sup>3</sup> Nowadays, with the most active catalysts the coupling of aryl boronic acids with aryl chlorides can be carried out at metal loadings of a few hundreds of

ppm.<sup>3d,4,5</sup> Particularly efficient systems can be successfully employed with aryl chlorides even at room temperature<sup>6</sup> and the presence of heteroatoms on the substrates is also tolerated.<sup>1g,7</sup>

The use of palladium catalysts containing P,O, P,N or P,S bidentate ligands<sup>3d,7c,8–12</sup> is a very interesting strategy because during the catalytic cycle the metal centre needs to accommodate in its coordination sphere species having different ligating abilities. For instance, we have recently reported that palladium complexes containing iminophosphine ligands such as **1** (Fig. 1) are efficient and versatile catalysts in the Suzuki,<sup>13</sup> Stille<sup>14</sup> and Heck<sup>15</sup> coupling reactions.

Although the catalysts based on ligand **1** efficiently activate a variety of aryl bromides, they were found ineffective with chlorides. As it is generally accepted that strongly basic and sterically

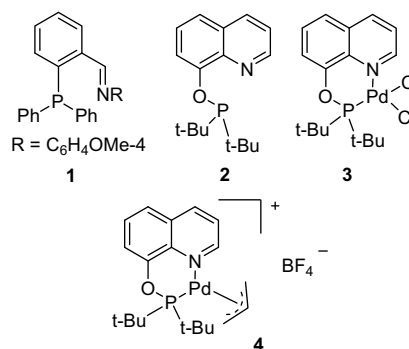


Figure 1. P,N ligands and palladium complexes active in Suzuki–Miyaura reaction.

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demanding ligands are required to activate the less reactive aryl–Cl bond, we attributed this failure to the modest basic and steric properties of the PPh<sub>2</sub> moiety of **1**. Aiming at developing more effective catalysts, we have synthesized the much more basic and sterically demanding P,N ligand **2** and the corresponding palladium(II) complexes **3** and **4** (Fig. 1).<sup>16</sup> In ligand **2** the bulky and strongly electron donating *tert*-butyl groups fulfil two functions: (i) increase the  $\sigma$ -donor ability of the P atom which promotes the oxidative addition of the substrate due to the increased electron density on the central metal, and (ii) increase the steric crowding around the metal which favours the reductive elimination step and stabilizes the labile Pd(0) intermediate. Furthermore, the 8-oxyquinoline moiety gives some  $\pi$ -acid character to the ligand and, according to Bedford work,<sup>3a</sup> this should promote the attack of the boronic acid on the metal centre. Hopefully, ligand **2** behaves in a hemilabile fashion through reversible rupture of the Pd–N bond thus favouring the approach of the boronic acid to the Pd(II) centre and, then, the reductive elimination step by pushing the organic fragments in mutual *cis* position. It is finally worth of note that even if the N atom of the quinoline group is a ‘hard’ donor it should be able to weakly coordinate the ‘soft’ Pd(0) centre contributing to stabilize the catalytically active species. Indeed, preliminary tests<sup>16</sup> showed that both **3** and **4** are very efficient catalysts for the Suzuki reaction being able to promote the coupling of phenylboronic acid with aryl bromides and even with aryl chlorides. Herein we wish to report the results of more detailed investigations into the potential of the new ligand.

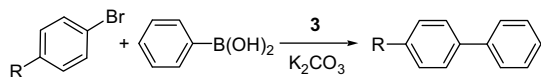
## 2. Results and discussion

Ligand **2** rapidly decomposes under aerobic conditions owing to simultaneous P oxidation and hydrolysis of the P–O bond, but it becomes stable when coordinated to a Pd(II) ion,<sup>16</sup> so that solutions of **3** and **4** in toluene or other organic solvents can be handled safely in air at room temperature. As the preliminary experiments had shown that the catalytic activity of **4** is almost identical to that of **3**,<sup>16</sup> only this latter complex was employed in this study.

To evaluate the catalytic efficiency of **3** and optimize the reaction conditions, we chosen as the model reactions the couplings of phenylboronic acid with 4-bromoacetophenone or bromobenzene, the former compound chosen as the representative of electronically activated substrates and the latter as the representative of the inactivated ones.

Table 1 shows the results obtained in a series of isochronous experiments in which the catalyst loading was progressively

**Table 1**  
Suzuki–Miyaura coupling of phenylboronic acid with bromoacetophenone or bromobenzene<sup>a</sup>



Entry	R	ArBr/ <b>3</b>	Conv. [%] <sup>b</sup>	TON <sup>c</sup>	TOF [h <sup>-1</sup> ] <sup>d</sup>
1	CH <sub>3</sub> CO	100,000	99	99,000	50,000
2	H	100,000	99	99,000	50,000
3	CH <sub>3</sub> CO	200,000	95	190,000	95,000
4 <sup>e</sup>	CH <sub>3</sub> CO	200,000	31	62,000	31,000
5	H	200,000	94	188,000	94,000
6	CH <sub>3</sub> CO	400,000	94	376,000	188,000
7	H	400,000	79	316,000	158,000
8	CH <sub>3</sub> CO	800,000	29	232,000	116,000
9	H	800,000	21	168,000	84,000

<sup>a</sup> Reaction conditions: solvent: toluene (12 mL); T: 110 °C; t: 2 h; ArBr: 4.0 mmol; phenylboronic acid: 6.0 mmol; K<sub>2</sub>CO<sub>3</sub>: 8.0 mmol; acid/ArBr=1.5:1; K<sub>2</sub>CO<sub>3</sub>/ArBr=2:1.

<sup>b</sup> By GLC with *n*-undecane as internal standard.

<sup>c</sup> Mol of ArBr converted/mol of catalyst.

<sup>d</sup> Mol of ArBr converted/mol of catalyst per hour.

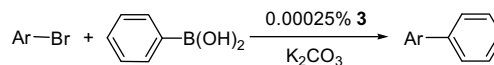
<sup>e</sup> Reaction under aerobic conditions.

reduced. The experiments showed that **3** is highly active: in fact, with 4-bromoacetophenone the substrate to catalyst ratio can be increased from 100,000:1 to 400,000:1 with almost complete substrate conversion and with TOF values of up to 190,000 h<sup>-1</sup>. Even with an inactivated substrate such as bromobenzene, conversions higher than 90% can be obtained in only two hours using catalyst loadings as low as 5 ppm.

This result is of particular interest because the use of low catalyst loadings is profitable only when high reaction rates are accompanied by almost complete conversions since otherwise expensive procedures for the separation of the products from the substrates would be required. Interestingly, high TON values are obtained even when the substrate to palladium ratio is increased to 800,000:1. However, at these very low catalyst loadings the reaction rate decreases; this effect is to be ascribed either to the increasing importance of impurities present in the substrates or to side reactions leading to deactivation of the catalyst. In this connection it is to mention that an experiment carried out under aerobic conditions (entry 4 of Table 1) showed that at high temperature the catalytic system becomes air sensitive.

The data in Table 2 highlight the effect of substitution on the aryl bromide: the presence of small electron-donating moieties in *para* position on the aryl bromide does not influence significantly the catalytic activity: the coupling of 4-bromoanisole or 4-bromotoluene with phenylboronic acid proceeds to completion in 2 h even using a substrate/catalyst ratio of 400,000:1. Indeed, slightly higher reaction rates are observed with 4-bromotoluene or 4-bromoanisole than with bromobenzene or 4-bromoacetophenone. On the other hand, the data of entries 5 and 6 of Table 2 illustrate the remarkable decrease of catalyst activity observed with substituents such as the methyl group in *ortho* position or the *tert*-butyl group in *para* position which sterically hinder the substrate. This effect is to be related to the steric hindrance of the ligand P,N, which likely retards both the oxidative addition of ArBr to a palladium(0) species and even more the step in which the phenyl moiety is transferred from boron to palladium (i.e., the transmetallation step).<sup>13c</sup>

**Table 2**  
Suzuki–Miyaura coupling of substituted aryl bromides with phenylboronic acid<sup>a</sup>



Entry	ArBr	Conv. [%] <sup>b</sup>	TOF [h <sup>-1</sup> ] <sup>c</sup>
1		94	188,000
2		79	158,000
3		99	199,000
4		100	200,000
5		21	42,000
6		15	30,000

<sup>a</sup> Reaction conditions: solvent: toluene (12 mL); T: 110 °C; t: 2 h; ArBr/ **3**=400,000:1; ArBr: 4.0 mmol; phenylboronic acid: 6.0 mmol; K<sub>2</sub>CO<sub>3</sub>: 8.0 mmol; acid/ArBr=1.5:1; K<sub>2</sub>CO<sub>3</sub>/ArBr=2:1.

<sup>b</sup> By GLC with *n*-undecane as internal standard.

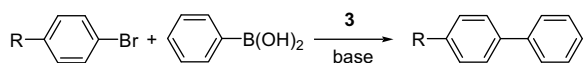
<sup>c</sup> Mol of ArBr converted/mol of catalyst per hour.

In order to optimize the reaction conditions a series of isochronous experiments was carried out changing the base, the reaction temperature and the nature of the solvent (see Table 3). For

the optimization of the base, a certain number of inorganic and organic species were tested in the coupling of 4-bromoacetophenone with phenylboronic acid in toluene using a substrate to palladium ratio of 100,000:1 at 110 °C. Serendipitously, K<sub>2</sub>CO<sub>3</sub>, the inexpensive inorganic base chosen for preliminary investigations, turned out to be the most efficient along with K<sub>3</sub>PO<sub>4</sub> which gives comparable results (entries 1–7 of Table 3), whereas organic bases such as triethylamine or sodium acetate are by far less efficient. It is interesting to note that by comparing the data in entries 1–3 and 4–5 a ‘potassium effect’ emerges, and it appears that the cation plays a key role in determining the efficiency of the base, similar effects have been previously observed by Bedford<sup>3a,d</sup> and Kwong.<sup>7c</sup>

**Table 3**

Influence of the base, of the temperature and of the solvent on the catalytic activity of complex **3**<sup>a</sup>



Entry	R	ArBr/3	Base	Solvent	T [°C]	Conv. [%] <sup>b</sup>
1	CH <sub>3</sub> CO	100,000	K <sub>2</sub> CO <sub>3</sub>	Toluene	110	99
2	CH <sub>3</sub> CO	100,000	Na <sub>2</sub> CO <sub>3</sub>	Toluene	110	19
3	CH <sub>3</sub> CO	100,000	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	110	23
4	CH <sub>3</sub> CO	100,000	K <sub>3</sub> PO <sub>4</sub>	Toluene	110	99
5	CH <sub>3</sub> CO	100,000	Na <sub>3</sub> PO <sub>4</sub>	Toluene	110	17
6	CH <sub>3</sub> CO	100,000	CH <sub>3</sub> COONa	Toluene	110	2
7	CH <sub>3</sub> CO	100,000	NEt <sub>3</sub>	Toluene	110	11
8	CH <sub>3</sub> CO	200,000	K <sub>2</sub> CO <sub>3</sub>	Toluene	110	94
9	H	200,000	K <sub>2</sub> CO <sub>3</sub>	Toluene	110	93
10	CH <sub>3</sub> CO	200,000	K <sub>2</sub> CO <sub>3</sub>	Toluene	100	63
11	H	200,000	K <sub>2</sub> CO <sub>3</sub>	Toluene	100	20
12	CH <sub>3</sub> CO	200,000	K <sub>2</sub> CO <sub>3</sub>	Toluene	90	16
13	H	200,000	K <sub>2</sub> CO <sub>3</sub>	Toluene	90	0
14	CH <sub>3</sub> CO	400,000	K <sub>2</sub> CO <sub>3</sub>	Toluene	110	94
15	CH <sub>3</sub> CO	400,000	K <sub>2</sub> CO <sub>3</sub>	DMF <sup>c</sup>	110	0
16	CH <sub>3</sub> CO	400,000	K <sub>2</sub> CO <sub>3</sub>	NMP <sup>d</sup>	110	0

<sup>a</sup> Reaction conditions: solvent: 12 mL; t: 2 h; ArBr: 4.0 mmol; phenylboronic acid: 6.0 mmol; base: 8.0 mmol; acid/ArBr=1.5:1; base/ArBr=2:1.

<sup>b</sup> By GLC using *n*-undecane as internal standard.

<sup>c</sup> DMF: *N,N*-dimethylformamide.

<sup>d</sup> NMP: *N*-methylpyrrolidinone.

The influence of the temperature was studied using both bromobenzene and 4-bromoacetophenone. The relevant data (entries 8–12 of Table 3) show that on lowering the temperature, the catalytic activity decreases sharply and at 90 °C only modest reaction rates are observed even with an activated substrate such as 4-bromoacetophenone. It is noteworthy that while at 110 °C the reaction rates for the two substrates are almost identical, at 100 or at 90 °C 4-bromoacetophenone reacts significantly faster than bromobenzene.

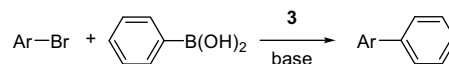
While at lower temperatures the rates decrease on going from 4-bromoacetophenone to bromobenzene, at 110 °C the reaction rates are almost independent on the electronic properties of the *para* group on the aryl bromide (see also entries 1–4 of Table 2). Possibly at 110 °C transmetallation is the rate-determining step in the catalytic cycle, whereas at 90 or 100 °C the reaction rate is controlled by the oxidative addition of the aryl bromide to the catalytically active Pd(0) species. Kinetic studies are currently in progress in order to confirm this hypothesis and gain a quantitative outline of the potassium effect found.

Finally, it is to mention that no catalytic activity was observed when toluene was replaced by DMF or NMP (entries 15 and 16 of Table 3); although we have no experimental data supporting a rationalization for this somehow outstanding result, we believe that these solvents could activate some process leading to decomposition of catalyst (e.g., ligand hydrolysis). Since toluene is an inexpensive and harmless solvent, no further experiment with high boiling, highly polar solvents was carried out.

Once optimized the reaction conditions, the coupling of hindered aryl bromides was more extensively investigated using catalyst loadings in the 50–200 ppm range. The reactions were carried out in toluene at 110 °C and both K<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub> were employed as bases. The results of selected experiments are reported in Table 4.

**Table 4**

Coupling of hindered aryl bromides with phenylboronic acid<sup>a</sup>



Entry	ArBr	ArBr/3	Base	Conv. [%] <sup>b</sup>
1		20,000	K <sub>2</sub> CO <sub>3</sub>	98
2		20,000	K <sub>3</sub> PO <sub>4</sub>	96
3		20,000	K <sub>2</sub> CO <sub>3</sub>	95
4		20,000	K <sub>3</sub> PO <sub>4</sub>	71
5		5000	K <sub>2</sub> CO <sub>3</sub>	98
6		5000	K <sub>3</sub> PO <sub>4</sub>	39
7		5000	K <sub>2</sub> CO <sub>3</sub>	98
8		5000	K <sub>3</sub> PO <sub>4</sub>	14

<sup>a</sup> Reaction conditions: solvent: toluene (12 mL); T: 110 °C; t: 2 h; ArBr: 4.0 mmol; phenylboronic acid: 6.0 mmol; base: 8.0 mmol; acid/ArBr=1.5:1; base/ArBr=2:1.

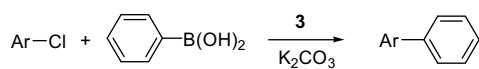
<sup>b</sup> By GLC with *n*-undecane as internal standard.

At a substrate to catalyst ratio of 20,000:1 the coupling of 1-bromo-4-*tert*-butylbenzene with phenylboronic acid can be carried out to almost complete conversion in only two hours with either base. On the other hand, with more hindered substrates K<sub>3</sub>PO<sub>4</sub> appears distinctly less efficient than K<sub>2</sub>CO<sub>3</sub>. In the presence of the latter base and with a catalyst loading of 50 ppm, the coupling of 1-bromo-2-methylbenzene with phenylboronic acid goes to completion in two hours. On further increasing the steric hindrance of the substrate, the catalytic activity decreases to such extent that for the coupling of 2-bromo-1,3-dimethylbenzene or 2-bromo-1,3,5-trimethylbenzene with phenylboronic acid it is necessary to increase the catalyst loading to 0.02 mol% in order to achieve an almost complete substrate conversion in 2 h.

Encouraged by these excellent results, we have investigated the catalytic activity of **3** in the coupling of phenylboronic acid with some simple aryl chlorides (Table 5).

Excellent activities were observed (entries 1–3) with substrates activated by EWG such as 4-chloroacetophenone (entries 1–2). Indeed, at a aryl chloride to catalyst ratio as high as 3000:1 the reaction goes to completion in about two hours; moreover, even using only a 0.02 mol% of catalyst the reaction reaches a 75% conversion in 2 h.

**Table 5**  
Coupling of phenylboronic acid with aryl chlorides<sup>a</sup>



Entry	ArCl	ArCl/3	Conv. [%] <sup>b</sup>	TON <sup>c</sup>
1		1000	100	1000
2		3000	96	2880
3		5000	75	3750
4		1000	53	530
5		1000	28	280
6		1000	17	170

<sup>a</sup> Reaction conditions: solvent: toluene (12 mL); T: 110 °C; t: 2 h; ArCl: 4.0 mmol; phenylboronic acid: 6.0 mmol; K<sub>2</sub>CO<sub>3</sub>: 8.0 mmol; acid/ArCl=1.5:1; base/ArCl=2:1.

<sup>b</sup> By GLC with *n*-undecane as internal standard.

<sup>c</sup> Mol of ArCl converted/mol of catalyst.

In contrast with that found with aryl bromides, the presence of EDG in *para* position on the aryl chloride significantly influences the catalysis leading to reduced reaction rates. This effect suggests that with aryl chlorides the oxidative addition of the substrate to the metal centre is the rate determining step in the catalytic cycle.

### 3. Conclusions

In summary, complex **3** is a highly efficient catalyst for the Suzuki–Miyaura coupling. The reaction can be carried out in toluene using inexpensive bases such as K<sub>2</sub>CO<sub>3</sub> or K<sub>3</sub>PO<sub>4</sub>. With aryl bromides very high TOF numbers can be obtained and, interestingly, the presence of EDG on the substrate does not affect the reaction rate. At variance, the catalytic activity decreases significantly with aryl bromides bearing bulky substituents; however, the catalyst is so efficient that the coupling of 2-bromo-1,3,5-trimethylbenzene with phenylboronic acid can be carried out with quantitative yield using 0.02 mol% in only two hours. Lower reaction rates are obtained with aryl chlorides, but still the catalyst activity is excellent. In contrast with that found with aryl bromides, the presence of EDG in *para* position of the aryl chlorides leads to significantly reduced reaction rates. By comparison with the most active catalysts it appears that **3** suffers of some limitations in particular when hindered substrates are used. We are prone to attribute this weakness to the stiffness of the 8-oxyquinoline moiety, future work to improve the ligand design is planned.

## 4. Experimental

### 4.1. General materials and methods

The catalytic experiments were carried out under argon atmosphere using standard Schlenk techniques, unless otherwise stated. Toluene was distilled over sodium/benzophenone under argon and immediately used. DMF and NMP were purified as described in the literature.<sup>17</sup> Bromobenzene (Aldrich) was distilled immediately before the use, the other aryl halides were high purity commercial products (Aldrich) and were used as received. Complex **3** was prepared as described previously.<sup>16</sup> The coupling products were

identified by their GC–MS and <sup>1</sup>H NMR. <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) were recorded on a Bruker Avance 300 spectrometer operating at 300.11 MHz. GC–MS spectra were obtained with a HP 5890 series II gas chromatograph interfaced to a HP 5971 quadrupole mass detector. The catalytic reactions were monitored by GLC on an Agilent Technologies 6850 gas chromatograph.

### 4.2. General procedure for coupling reactions

In a typical experiment (entry 6 of Table 1), a 50 mL glass reactor was charged with 4-bromoacetophenone (0.80 g, 4.0 mmol), phenylboronic acid (0.73 g, 6.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1.10 g, 8.0 mmol), *n*-undecane (0.16 g, 1.0 mmol, as the gas chromatographic internal standard) and 12 mL of toluene. To the resulting suspension 100 μL of a 1.0 × 10<sup>-4</sup> mol/L solution of complex **3** in toluene were added and the mixture was heated under magnetic stirring at 110 °C for 2 h. After cooling to room temperature and filtration on Celite, the raw reaction mixture was analyzed by GLC.

## References and notes

- Recent reviews: (a) Miyaura, N. In *Metal-Catalyzed Cross-Coupling reactions*; 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Chapter 2; (b) Bellina, F.; Carpita, A.; Rossi, R. *Synthesis* **2004**, 2419; (c) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651; (d) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609; (e) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133; (f) Molander, G. A.; Ellis, N. *Acc. Chem. Res.* **2007**, *40*, 275; (g) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461; (h) Alonso, F.; Beletskaya, I. P.; Yus, M. *Tetrahedron* **2008**, *64*, 3047.
- Beller, M.; Fischer, H.; Herrmann, W. A.; Öfele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848.
- For selected references, see: (a) Bedford, R. B.; Hazelwood (née Welch), S. L.; Horton, P. N.; Hursthouse, M. B. *Dalton Trans.* **2003**, 4164; (b) Albiison, D. A.; Bedford, R. B.; Lawrence, S. E.; Noelle Scully, P. *Chem. Commun.* **1998**, 2095; (c) Bedford, R. B.; Welch, S. L. *Chem. Commun.* **2001**, 129; (d) Bedford, R. B.; Hazelwood (née Welch), S. L.; Limmert, M. E.; Albiison, D. A.; Draper, S. M.; Noelle Scully, P.; Coles, S. J.; Hursthouse, M. B. *Chem.—Eur. J.* **2003**, *9*, 3216; (e) Inés, B.; SanMartin, R.; Churrua, F.; Domínguez, E.; Urriaga, M. K.; Arriortua, M. I. *Organometallics* **2008**, *27*, 2833; (f) Kondolff, I.; Feuerstein, M.; Doucet, H.; Santelli, M. *Tetrahedron* **2007**, *63*, 9514.
- For reviews on the Pd-catalyzed couplings of aryl chlorides see: (a) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176; (b) Bedford, R. B.; Cazin, C. S. J.; Holder, D. *Coord. Chem. Rev.* **2004**, *248*, 2283.
- For selected references, see: (a) Bedford, R. B.; Cazin, C. S. J.; Hazelwood (née Welch), S. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 4120; (b) Bedford, R. B.; Hazelwood (née Welch), S. L.; Limmert, M. E. *Chem. Commun.* **2002**, 2610; (c) Schneider, S. K.; Roembke, P.; Julius, G. R.; Raubenheimer, H. G.; Herrmann, W. A. *Adv. Synth. Catal.* **2006**, *348*, 1862; (d) Zapft, A.; Ehrentraut, A.; Beller, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4153; (e) Zapft, A.; Jackstell, R.; Rataboul, F.; Riermeier, T.; Monsees, A.; Fuhmann, C.; Shaikh, N.; Dingerdissen, U.; Beller, M. *Chem. Commun.* **2004**, 38; (f) Colacot, T. J.; Shea, H. A. *Org. Lett.* **2004**, *6*, 3731; (g) So, C. M.; Lau, C. P.; Kwong, F. Y. *Org. Lett.* **2007**, *9*, 2795; (h) Fleckenstein, C. A.; Plenio, H. *Organometallics* **2007**, *26*, 2758; (i) Cui, M.; Li, J.; Yu, A.; Zhang, J.; Wu, Y. *J. Mol. Catal. A: Chem.* **2008**, *290*, 67.
- For selected references, see: (a) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101; (b) Navarro, O.; Kelly, R. A.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194; (c) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685 and references therein; (d) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020; (e) Liu, S.-Y.; Choi, M. J.; Fu, G. C. *Chem. Commun.* **2001**, 2408; (f) Gstöttmayr, C. W. K.; Böhm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1363.
- For selected references, see: (a) Billingsley, K.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3358 and references therein; (b) Li, F.; Hor, T. S. A. *Adv. Synth. Catal.* **2008**, *350*, 2391; (c) So, C. M.; Yeung, C. C.; Lau, C. P.; Kwong, F. Y. *J. Org. Chem.* **2008**, *73*, 7803; (d) Kondolff, I.; Doucet, H.; Santelli, M. *J. Mol. Catal. A: Chem.* **2007**, *269*, 110.
- A recent review on the use of bidentate P,O ligands: Kwong, F. Y.; Chan, A. S. C. *Synlett* **2008**, 1440.
- A recent review on the use of hemilabile ligands: Weng, Z.; Teo, S.; Hor, T. S. A. *Acc. Chem. Res.* **2007**, *40*, 676.
- Recent examples of bidentate P, O ligands employed in Suzuki reaction: (a) Dai, W.-M.; Li, Y. N.; Zhang, Y.; Yue, C. Y.; Wu, J. L. *Chem.—Eur. J.* **2008**, *14*, 5538; (b) Venkateswaran, R.; Balakrishna, M. S.; Mobin, S. M. *Eur. J. Inorg. Chem.* **2007**, 1930; (c) Singh, G.; Bali, S.; Singh, A. K. *Polyhedron* **2007**, *26*, 897; (d) Teo, S.; Weng, Z.; Hor, T. S. A. *Organometallics* **2006**, *25*, 1199.
- Recent examples of bidentate P,N ligands employed in Suzuki reaction: (a) Chiang, W. Y.; Hong, F. E. *J. Organomet. Chem.* **2009**, *694*, 1473; (b) Yu, S. B.; Hu, X. P.; Deng, J.; Huang, J. D.; Wang, D. Y.; Duan, Z. C.; Zheng, Z. *Tetrahedron Lett.* **2008**, *49*, 1253; (c) Kingston, J. V.; Verkade, J. G. *J. Org. Chem.* **2007**, *72*, 2816; (d)

- Kühnert, J.; Dušek, M.; Demel, J.; Lang, H.; Štěpnička, P. *Dalton Trans.* **2007**, 2802; (e) Guo, M. P.; Jian, F. F.; He, R. *Tetrahedron Lett.* **2006**, 47, 2033; (f) Weng, Z.; Teo, S.; Koh, L. L.; Hor, T. S. A. *Organometallics* **2004**, 23, 4342.
12. Recent examples of bidentate P,S ligands employed in Suzuki reaction: (a) Punji, B.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2006**, 45, 9454; (b) Punji, B.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2007**, 46, 11316; (c) Zhang, W.; Shi, M. *Tetrahedron Lett.* **2004**, 45, 8921.
13. (a) Scrivanti, A.; Beghetto, V.; Matteoli, U.; Antonaroli, S.; Marini, A.; Mandoj, F.; Paolesse, R.; Crociani, B. *Tetrahedron Lett.* **2004**, 45, 5861; (b) Scrivanti, A.; Beghetto, V.; Matteoli, U.; Antonaroli, S.; Marini, A.; Crociani, B. *Tetrahedron* **2005**, 61, 9752; (c) Crociani, B.; Antonaroli, S.; Marini, A.; Matteoli, U.; Scrivanti, A. *Dalton Trans.* **2006**, 2698.
14. Crociani, B.; Antonaroli, S.; Beghetto, V.; Matteoli, U.; Scrivanti, A. *Dalton Trans.* **2003**, 2194.
15. Scrivanti, A.; Bertoldini, M.; Matteoli, U.; Beghetto, V.; Antonaroli, S.; Marini, A.; Crociani, B. *J. Mol. Catal. A: Chem.* **2005**, 235, 12.
16. Crociani, B.; Antonaroli, S.; Burattini, M.; Benetollo, F.; Scrivanti, A.; Bertoldini, M. *J. Organomet. Chem.* **2008**, 693, 3932.
17. Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; 4th ed.; Butterworth-Heinemann: Oxford, 1996.