Ferrocenyl phosphine–oxazaphospholidine oxide ligands for the Suzuki–Miyaura coupling of hindered aryl bromides and chlorides[1]

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Abstract: A series of ferrocenyl oxazaphospholidine phosphines that differ electronically and sterically were investigated as ligands for the Suzuki–Miyaura cross-coupling reactions. One of these compounds, **1**, was shown to be highly effective in the coupling reactions of bulky aryl bromides with boronic acids when combined with $Pd(OAc)_2$, while another, **2**, was capable of coupling aryl chlorides with boronic acids. However, these ligands were less effective in asymmetric induction.

Key words: Suzuki–Miyaura coupling, ferrocenyl phosphines, aryl bromides, aryl chlorides, palladium.

Résumé : Une série de ferrocényl oxazaphospholidine phosphines qui présentent des différences tant électroniques que stériques a été étudiée comme ligands pour les réactions de couplage croisé de Suzuki–Miyaura. On a montré qu'un de ces composés, **1**, lorsqu'il est combiné au $Pd(OAc)_2$, est très efficacle dans les réactions de couplage de bromures d'aryles avec des acides boroniques alors que le composé **2** permet d'effectuer le couplage de chlorures d'aryles avec les acides boroniques. Toutefois, ces ligands sont moins efficaces dans l'induction asymétrique.

Mots-clés : couplage de Suzuki–Miyaura, ferrocényl phosphines, bromures d'aryles, chlorures d'aryles, palladium.

[Traduit par la Rédaction]

Introduction

The palladium-catalyzed cross-coupling reactions of organoboron compounds and organic halides or triflates have emerged as a powerful and general methodology for the formation of carbon–carbon bonds (1–7). Advances in recent years have made the reactions scalable and cost effective (8). However, methods that are generally applicable to the synthesis of bulky and axially chiral biaryls, common structural motifs in natural products and chiral ligands, are still rare (9–17). Although reasonably good results in the enantioselective Suzuki coupling have been achieved using P^N ligands based on biaryl and ferrocene backbones, the reaction times, scope of substrates, and catalyst loadings remain to be improved (18, 19).

Suzuki–Miyaura coupling of hindered aryl bromides and chlorides is a particularly challenging area of research. Recently, new and improved catalytic systems for the coupling of these demanding substrates have been developed and described (20–28). In particular, biaryl monophosphine ligands have proven to be highly effective, partially meeting the requirement of increased catalytic performance (29). However, there remain some key issues that need to be addressed; these include problems such as hydrolysis of Pd–Ar complexes, slow transmetalation or slow trans to cis isomerization of intermediate palladium species, leading to the formation of unwanted byproducts (18, 29–34).

Ferrocene-based ligands have been employed successfully in many catalytic transformations (35) due to their ease of functionalization and the stability of most of its derivatives. Its proven record in homogeneous catalysis has been demonstrated. The Suzuki–Miyaura reaction is no exception to this trend (36, 37). Recently, we reported a new series of ferrocenyl-phosphine ligands that were synthesized by ortholithiation of (2*R*,4*S*,5*R*)-3,4-dimethyl-2-ferrocenyl-5-phenyl-[1,3,2]oxazaphospholidine 2-oxide (Scheme 1) (38). Herein, we present our findings on the application of the ligands **1**–**4** in the Suzuki–Miyaura reactions.

Received 27 March 2008. Accepted 30 May 2008. Published on the NRC Research Press Web site at canjchem.nrc.ca on 3 September 2008.

Dedicated to Professor Dick Puddephatt for his outstanding contributions to chemistry and mentoring.

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[1]This article is part of a Special Issue dedicated to Professor R. Puddephatt.
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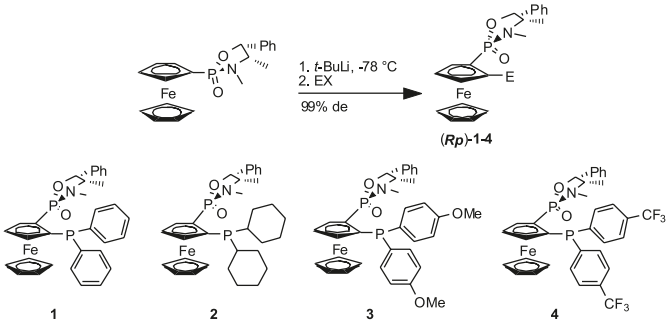
 doi:10.1139/V08-113

Scheme 1. Ferrocenyl phosphino ligands synthesized by ortho-lithiation and examined in this study.



Experimental[3]

Procedures for Suzuki–Miyaura coupling reactions

The coupling of 1-bromo-2-methoxynaphthalene with 1-naphthalene boronic acid to give 2-methoxy-1,1′-binaphthyl, **5**, is described as a typical example. An oven-dried carousel reaction tube was charged with 1-naphthalene boronic acid (0.75 mmol), CsF (1.5 mmol), **1** (10 μmol), and $Pd(OAc)_2$ (5 μmmol). The aryl bromide (0.5 mmol) was introduced at this stage (or after degassing by injection through a rubber septum in case of a liquid). The reaction vessel was evacuated and backfilled with N_2. This process was repeated five times, after which dioxane (3 mL) was introduced. The reaction mixture was then heated at 100 °C for 4 h. After cooling down to ambient temperature, the conversion was determined from the crude ^{1}H NMR, and isolated yield was obtained after a standard work-up and purification by flash chromatography (100% hexane). The product 2-methoxy-1,1′-binaphthyl, **5**, was obtained in 98% yield. Analytic details: mp 106 to 107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 3.75 (s, 3H), 7.14 (d, 1H, J = 8.8 Hz), 7.19–7.28 (m, 2H), 7.30–7.33 (m, 2H), 7.42–7.47 (m, 3H), 7.61 (t, 1H, J = 7.7 Hz), 7.86 (d, 1H, J = 8.0 Hz), 7.93 (d, 1H, J = 8.0 Hz), 7.94 (d, 1H, J = 8.0 Hz), 7.97 (d, 1H, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 56.8, 113.8, 123.2, 123.5, 125.5, 125.5, 125.7, 125.8, 126.2, 126.4, 127.7, 127.8, 128.2, 128.4, 129.0, 129.4, 132.9, 133.7, 134.2, 134.5, 154.6. MS *m/z*: 284 (M^+). The products **6**–**19** were obtained in a similar manner.

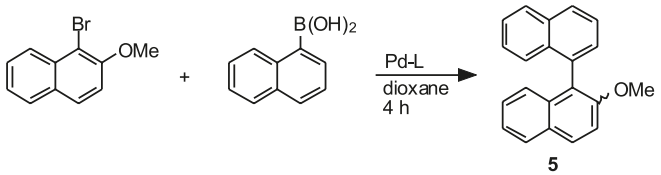
X-ray structural determination of Pd-1

The complex **Pd-1** was synthesized by heating $PdCl_2(PhCN)_2$ with **1** in dry dichloromethane with a 91% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 0.78 (s, br, 3H), 2.00 (d, 3H, J = 11.2 Hz), 3.69 (m, 1H), 4.15 (br, 1H), 4.75 (s, 5H), 4.80 (br, 1H), 4.83 (br, 1H), 5.70 (br, 1H), 7.30–7.90 (m, 15H). ^{31}P NMR ($CDCl_3$, 162 MHz, ppm) δ: 16.4(s), 46.6(s). HR-MS (ES+) *m/z*: calcd. for $C_{32}H_{31}{}^{37}Cl^{54}FeNO_2P_2Pd$: 719.9920, $C_{32}H_{31}{}^{35}Cl^{56}FeNO_2P_2Pd$: 719.9903 $[M - Cl]^+$; found: 719.9918.

Single crystal X-ray data were collected on a Bruker D8 diffractometer with an APEX detector using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). The crystal was cooled to T = 110(2) K. A total of 19537 reflections was collected with $2\theta_{max}$ = 55.1°. Of these reflections, 13146 were unique (R_{int} = 0.0406). The reflection data were integrated using SAINT v6.45a (39). The data were corrected for absorption, decay, and other errors using SADABS V2007-2 (40). The structure was solved by direct methods and refined using SHELX (41). X-SEED (42), a graphical interface to SHELX, was used to generate representations of the crystal structure.

Crystal data: $2(C_{32}H_{31}Cl_2FeNO_2P_2Pd)$, C_7H_5N, $CHCl_3$, M = 1701.38, orange block, 0.20 mm × 0.20 mm × 0.10 mm, monoclinic, space group $P2_1$ (No. 4), a = 9.4590(19), b = 19.219(4), c = 19.677(4) Å, β = 96.99(3)°, V = 3550.5(12) Å^3, Z = 2, $D_{calcd.}$ = 1.591 g/cm^3, F_{000} = 1720. Final GoF = 1.011, $R1$ = 0.0517, $wR2$ = 0.1042, R indices based on 10244 reflections with $I > 2\sigma(I)$ (refinement on F^2), 842 parameters, 1 restraint, μ = 1.266 mm^{-1}. Absolute structure parameter = –0.00(2).

Table 1. Suzuki coupling with $Pd(OAc)_2$ and ligands **1**–**4**.



Entry	Ligand	L/Pd ratio	Conv. (%)	Yield (%)[a]
1	**1**	2	>99	98
2	**1**	1	78	63
3	**2**	2	55	50
4	**2**	1	>99	94
5	**3**	2	91	90
6	**3**	1	78	76
7	**4**	2	97	91
8	**4**	1	90	79
9[b]	**1**	2	61	54
10[b]	**2**	1	27	21
11[b]	**3**	2	39	22
12[b]	**4**	2	53	39
13	$FcPPh_2$	2	22	8

Note: Reaction conditions: 1.0 equiv. of aryl bromide, 1.5 equiv. of boronic acid, 3.0 equiv. of CsF, 1 mol% $Pd(OAc)_2$, 105 °C, 4 h in dioxane.

[a]Isolated yields; hydrolysis products were observed in the case of low yields.

[b]Reaction time: 1 h.

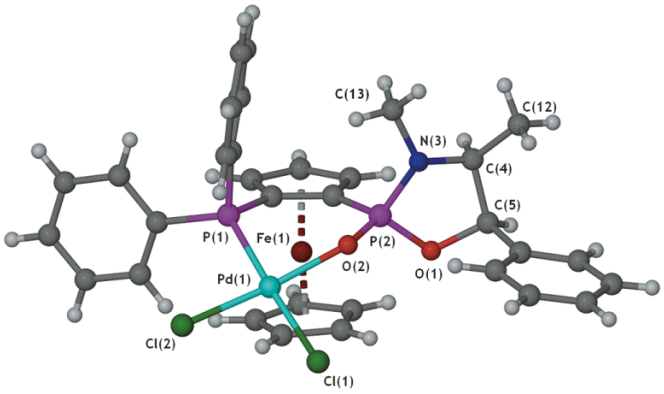
Results and discussion

Ligand screening

The ligands **1**–**4** are hemilabile, with P^O chelation to Pd being the most likely. Sterically and electronically, however, they show different behaviour, and it was of interest to see

[3] Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3800. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC 691402 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Fig. 1. The X-ray structure of **Pd-1**. Selected bond distances (Å) and angles (°): Pd(1)–O(2) 2.071(4), Pd(1)–P(1) 2.229(2), Pd(1)–Cl(2) 2.262(2), Pd(1)–Cl(1) 2.364(2); O(2)-Pd(1)-P(1) 88.93(14), O(2)-Pd(1)-Cl(2) 172.8(1), P(1)-Pd(1)-Cl(2) 89.94(7), O(2)-Pd(1)-Cl(1) 88.4(1), Cl(2)-Pd(1)-Cl(1) 92.77(7).

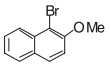
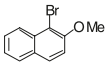
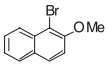
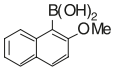
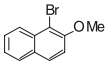
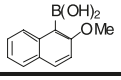


how this difference would impact the palladium-catalyzed Suzuki coupling. At the outset, we examined the coupling between the sterically hindered 1-bromo-2-methoxynaphthalene and 1-naphthalene boronic acid and compared the results with a similar but less bulky phosphine. The results are reported in Table 1.

As can be seen, ligand **1** showed excellent results when the ligand/catalyst ratio was set to 2. The reaction was complete after 4 h and the coupling product was recovered in 98% yield after purification by column chromatography (Table 1, entry 1). At a lower concentration of ligand, the reaction slowed down, lowering the yield to 63% (Table 1, entry 2). In contrast, the reaction with ligand **2** was found to go to completion when a 1/1 ligand/palladium (L/Pd) ratio was used (Table 1, entry 4). At higher concentrations, the rate dropped dramatically (Table 1, entry 3). Ligands **3** and **4** show similar behaviour and their results are somewhat similar to those obtained with the ligand **1**. To better appreciate the differences among the ligands, the coupling time was reduced. As is seen from the entries 9–12 in Table 1, the ligand **1** gave the best yields, and it appears that an electron rich phosphine does not benefit the coupling. The coupling was considerably less efficient with the less bulky ligand $FePPh_2$ (Fc = ferrocenyl) (Table 1). Thus, the oxazaphospholidine moiety of **1**–**4**, in combination with the phosphine group, is able to stabilize the active palladium species and accelerate the reaction rate. The differences between **1** and **2** could partially be explained by assuming a stable, active Pd species requires two equivalents of **1** but only one equivalent of the bulkier **2** (43).

The X-ray crystal structure of the complex, **Pd-1**, formed between **1** and $PdCl_2(PhCN)_2$, confirms that **1** behaves as a chelating ligand, with both the phosphorus atom and the phosphoryl oxygen atom of the oxazaphospholidine ring coordinating to the Pd(II) centre (Fig. 1). The compound crystallizes in the chiral space group $P2_1$ with 2 **Pd-1** molecules, a benzonitrile, and a chloroform molecule in the asymmetric unit, but the two organometallic molecules are chemically and nearly structurally identical. Examination of the orientation of the two molecules and the crystal packing reveals no missing symmetry elements, and the refined absolute structure parameter is further evidence that the crystals are indeed chiral. The molecular structure of one of the two molecules is shown in Fig. 1. The coordination geometry about the Pd(II) atom is square planar, with P, O, and the two Cl atoms cis to each other. The two Pd–Cl bonds are noticeably different [2.262(2) and 2.364(2) Å]. The longer Pd–Cl bond, which is trans to P(1), is likely to be due to the stronger trans effect of a P atom than an O atom. The three chiral centres of P(2), C(4), and C(5) have *R*, *S*, and *R* configurations, respectively. The complex is also planar chiral with a *R* configuration.

Table 2. Suzuki coupling of sterically hindered partners with **1**.

Entry	ArBr	$ArB(OH)_2$	Yield (%)	Product
1			98	**5**
2			93	**6**
3			91	**7**
4			97	**8**
5			97	**9**
6			96	**10**
7			12[a]	**11**
8			43[a,b]	**11**

Note: Reaction conditions: 1.0 equiv. of aryl bromide, 1.5 equiv. of boronic acid, 3 equiv. of CsF, 100 °C in dioxane, 1 mol% $Pd(OAc)_2$, 2 mol% **1**. Yield refers to isolated yields.

[a]Hydrolysis product was observed.

[b]NEt_3 (3 equiv.) and toluene as solvent were used.

During the Suzuki coupling, the phosphoryl oxygen could dissociate from the palladium to facilitate the transmetalation and recoordinate to induce a faster reductive elimination. This may well be the case with the bulkier **2**. In the case of **1**, **3**, and **4**, however, the need for 2 equiv. of ligand for a more efficient coupling appears to suggest that the phosphoryl oxygen is replaced by the phosphine group of a second ligand.

Aryl bromides as substrates

One of the biggest challenges in the use of a Suzuki–Miyaura reaction is the coupling of hindered substrates. Since the ligand **1** afforded the best results in the coupling of 1-bromo-2-methoxynaphthalene and 1-naphthalene boronic acid, its catalytic activity towards other hindered substrates was studied. The results of the coupling of various sterically

Table 3. Suzuki coupling of aryl chlorides using **2**.

Entry	ArCl	$ArB(OH)_2$	Time (h)	Yield (%)	Product
1			1	96	**12**
2			18	96[a]	**12**
3			8	92	**13**
4			8	93	**14**
5			8	93	**15**
6			8	97	**16**
7			8	91	**17**
8			24	97	**18**
9			24	84	**19**
10			24	89	**7**

Note: Reaction conditions: 1.0 equiv. of aryl chloride, 1.5 equiv. of boronic acid, 3.0 equiv. of CsF, 105 °C in dioxane, 1 mol% $Pd(OAc)_2$, 1 mol% ligand **2**. Yield refers to isolated yields.
[a]$Pd(OAc)_2$ (0.1 mol%).

hindered aryl bromides and sterically hindered aryl boronic acids employing ligand **1** are reported in Table 2.

The couplings involving the formation of the trisubstituted biaryls proceeded smoothly to completion. The reactions were complete after 4 h and no hydrolysis byproducts were observed in the crude mixtures. However, the reaction leading to tetra-substituted biaryl compounds resulted in low yields (Table 2, entries 7 and 8), and a significant amount of hydrolysis product, 2-methoxynaphthalene.

The important factor that impedes the coupling of partners in entry 7 of Table 2 is likely to be the increased steric bulk of the boronic acid, which makes the transmetallation difficult. This may in turn give preference to protonolysis of the Pd–Ar intermediate, leading to the hydrolysis product. Accordingly, a combination of CsF and NEt_3 as base and a nonprotic solvent like toluene afforded some improvement in the conversion. The yield increased from 12% to 43% (Table 2, entry 8), although 2-methoxynaphthalene was still observed.

Aryl chlorides as substrates

To find the best ligand for these substrates, we screened the ligands **1–4** for the coupling of the activated 4-chloroacetophenone with phenylboronic. In sharp contrast to the coupling of the bromides, only the ligand **2** was found to give satisfactory results; hence, the other ligands were not studied further. Apparently, a more electron-rich ligand is needed for the aryl chlorides, which are expected to be less reactive in the oxidative addition at Pd(0) than the corresponding bromides. The results of the coupling reactions obtained with **2** are summarized in Table 3.

The reaction between 4-chloroacetophenone and phenylboronic acid at 105 °C using 1 mol% of Pd and 1 equiv. of **2** was complete in just 1 h (Table 3, entry 1). Reducing the amount of palladium to 0.1 mol% resulted in a predictable decrease of the reaction rate; complete conversion was reached after 18 h (Table 3, entry 2). Increasing the steric bulk on the boronic acid also resulted in a decrease in the reaction rate (Table 3, entry 3). Although the coupling of the 4-chloroacetophenone with 2-tolylboronic acid also occurred at a 0.1 mol% Pd loading, the reaction took more than one day to reach completion. The rest of the reactions were therefore performed using 1 mol% Pd.

As can be seen from Table 3, going from an activated chloride to a deactivated one like 2-chlorotoluene, the yield was not affected under the conditions employed. The coupling of sterically hindered boronic acids, such as 1-naphthylboronic acid and 2-tolylboronic acid (Table 3, entries 6 and 7), ran smoothly to completion after 8 h. However, a further increase in the steric bulk of the chlorides did eventually affect the reaction rate. Thus, with 2-chloro-meta-xylene as substrate, the coupling reactions went to completion only after 24 h (entries 8–10). The results obtained with **2** are better than or comparable with those obtained using related electron-rich ferrocenyl phosphines (44, 45).

Table 4. Asymmetric Suzuki coupling.

Entry	Ligand	L/Pd	T (°C)	Time (h)	Conv. (%)	Ee (%)[a]
1	**1**	2	70	12	85	26 (*R*)
2	**1**	1	50	12	78	18 (*R*)
3	**2**	1	50	12	55	7 (*S*)
4	**2**	1	70	12	>99	9 (*S*)
5	**2**	2	70	7	80	27 (*R*)
6	**3**	2	70	12	84	14 (*R*)
7	**4**	2	70	12	92	3 (*R*)

Note: Reaction conditions: 1.0 equiv. of aryl bromide, 1.5 equiv. of boronic acid, 3.0 equiv. of CsF, dioxane, 5 mol% $Pd(OAc)_2$.
[a]Determined by HPLC using a DAICEL OJ column (90/10 hexane/iPrOH).

Asymmetric coupling

So far, few catalysts have been developed for asymmetric Suzuki cross-coupling reactions (18, 19). In the course of this study, we examined the ligands **1–4** for the asymmetric coupling of 1-naphthylboronic acid and 1-bromo-2-methoxynaphthylboronic acid. The reaction conditions are slightly different from the ones reported in Table 1. The conversions and ee values obtained are reported in Table 4.

Ligand **1** yielded a 85% conversion and 26% ee as its best results (Table 4, entry 1). Decreasing the temperature or the L/Pd ratio did not bring about any amelioration. Although the ligand **2** was previously found to give a higher activity using a lower L/Pd ratio (Table 1, entry 4), it gave a higher enantioselectivity (27% ee) when 2 equiv. of the ligand were used (Table 4, entry 5). Most notably, the configuration of the product was reversed in the case of the latter, suggesting that the active catalyst varies with the L/Pd ratio. The higher ee for the L/Pd ratio of 2 is probably due to

the formation of a Pd-diphosphine species, which increases the steric bulk around the palladium. Ligand **4**, the electron-poor analogue of **1**, afforded the poorest enantioselectivity, which may partly stem from its ease of dissociation from the metal centre. However, it is difficult to draw conclusions relating the electronic and steric properties of ligand with the asymmetric induction observed, not least because there are probably more than one active catalytic species operating in the reaction media.

Conclusion

This paper presents results on the application of a series of electronically and sterically varied ferrocenyl ligands to the Suzuki–Miyaura cross-coupling reactions of aryl bromides and chlorides. Ligands **1** and **2** were proven to generate very effective catalysts for the coupling of sterically hindered partners. However, ligand **1** was ineffective in the coupling of aryl chlorides. For these substrates, including deactivated ones, the bulkier, electron-rich ligand **2** was necessary. A strong dependence of the catalytic activity on the L/Pd ratio was observed and this varied with the nature of the ligand. In contrast with **1**, an active catalyst was formed when 1 equiv. of **2** relative to the palladium was used, a scenario reminiscent of those observed with other bulky, electron-rich phosphines (43). The satisfying performance of the ligands in terms of reaction rates and substrate scope could partly be ascribed to the presence of the oxazaphospholidine moiety, which renders the ligand to be potentially hemilabile during the catalysis, thereby stabilizing the active palladium species. These ligands were also shown to induce enantioselection in the Suzuki coupling reaction; however, their performance remains to be improved in this respect.

Acknowledgements

We gratefully acknowledge Johnson Matthey and the Fundação para a Ciência e a Tecnologia (SFRH/BD/17262/2004 NM) for financial support.

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