

# Suzuki cross-coupling in aqueous media catalyzed by a 1,1'-*N*-substituted ferrocenediyl Pd(II) complex

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Received 24 July 2003; accepted 15 September 2003

## Abstract

Reaction of PdCl<sub>2</sub>(MeCN)<sub>2</sub> with Fe[η-C<sub>5</sub>H<sub>4</sub>NC(H)Ph-N]<sub>2</sub> (**1**) at MeOH at r.t. gives air-stable PdCl<sub>2</sub>Fe[η-C<sub>5</sub>H<sub>4</sub>NC(H)Ph-N]<sub>2</sub> (**2**; yield 84%). X-ray single-crystal diffraction analyses show that **2** is a Pd(II) square planar complex with *N,N'* chelation of the ferrocenediyl ligand, without Fe–Pd bond. It effectively catalyzes Suzuki cross-coupling reactions of aryl iodides and bromides with aryl boronic acids in aqueous media under non-homogeneous conditions in which the products can be easily isolated. The reaction conditions including choice of base, catalytic load and catalyst recoverability have been investigated and reported.

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**Keywords:** 1,1'-Ferrocenediyl; Palladium; Catalysis; Aqueous; Suzuki coupling

## 1. Introduction

Palladium-catalyzed Suzuki cross-coupling of haloarenes with arylboronic acid has wide-ranging applications in organic synthesis [1]. In most cases, phosphine-stabilized catalysts are used. These are largely toxic [2] and organic-based. We are interested in developing a new generation of environmentally friendly water-based and phosphine-free catalysts of high efficiency. Since the products from these reactions are essentially water-insoluble, their separation and isolation as well as the catalyst recover process can also be conveniently achieved. Similar Pd-initiated reactions in aqueous media began to appear in the literature only very recently [3].

We have been focusing on the chemistry of 1,1'-bis(diphenylphosphino)ferrocene (dppf) (see for example [4]) largely because of its coordinative adaptability [5] and catalytic potential [6]. The recent elegant works of Arnold et al. on the improved synthesis of 1,1'-diaminoferrocene [7] and Gibson et al. [8] on its

conversion to 1,1'-*N*-substituted ferrocenediyl ligand, **1**, caught our attention. The latter ligand, although water-insoluble, fulfils at least three of our criteria, namely, phosphine-free, ferrocenyl-base, and coordinatively mobile. We therefore set out to examine its coordination ability to Pd(II) and the catalytic potential of the resultant complex.

## 2. Results and discussion

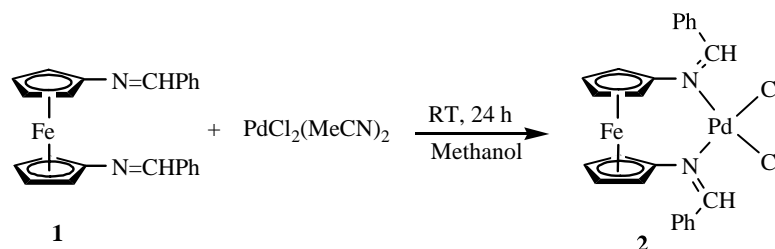
### 2.1. Structure, efficiency and advantages

The reaction between PdCl<sub>2</sub>(MeCN)<sub>2</sub> and **1** proceeds smoothly at MeOH at r.t. giving air-stable PdCl<sub>2</sub>Fe[η-C<sub>5</sub>H<sub>4</sub>NC(H)Ph-N]<sub>2</sub>, **2** (Scheme 1).

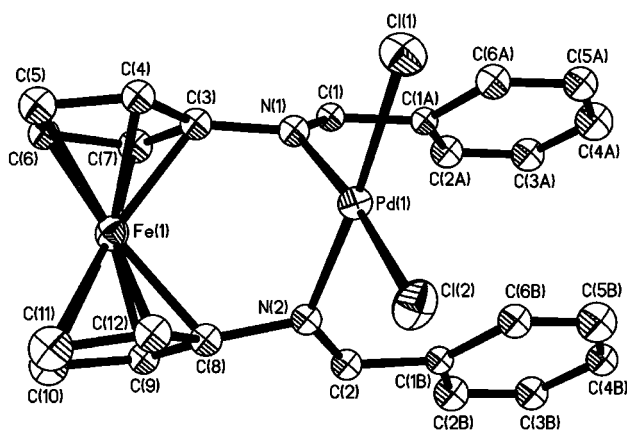
Single-crystal crystallographic analysis of **2** revealed the expected Pd(II) square planar complex with *N,N'* chelation of the ferrocenediyl ligand. The unit cell of **2** contains two independent molecules (A and B). The molecule A is shown in Fig. 1. Selected bond parameters are given in Table 1. The benzaldehyde imine functionality is within proximity but shows no apparent interaction with the metal center (the C–N bonds (1.290(15) and 1.309(15) Å) retain their double bond character).

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Scheme 1.

Fig. 1. Molecular structure *A* of complex **2**. Thermal ellipsoids are drawn at the 50% probability level.Table 1  
Selected bond lengths (Å) and angles (°) for **2**

	Mol. A	Mol. B
Pd(1)–N(1)	2.056(10)	2.066(11)
Pd(1)–N(2)	2.023(11)	2.077(12)
Pd(1)–Cl(1)	2.284(4)	2.301(4)
Pd(1)–Cl(2)	2.291(3)	2.287(4)
C(1)–N(1)	1.290(15)	1.228(15)
C(2)–N(2)	1.309(15)	1.237(17)
C(3)–N(1)	1.409(16)	1.436(16)
C(8)–N(2)	1.443(17)	1.440(17)
Cl(1)–Pd(1)–Cl(2)	90.27(14)	90.90(13)
N(1)–Pd(1)–N(2)	84.5(4)	84.5(4)
Cl(1)–Pd(1)–N(1)	93.1(3)	91.1(3)
Cl(2)–Pd(1)–N(2)	91.8(3)	93.0(3)
Two Cp's dihedral	7.3(3)	5.7(3)

The ferrocenediyl moiety is significantly skewed, with the Cp rings tilted inward at 7.3(3)°, in order to adapt to the chelate structure with short Pd–N bonds (2.056(10), 2.023(11) Å).

Since PdCl<sub>2</sub>(dppf) is one of the most established active C–C coupling catalysts and that much of its catalytic functions could be related to its stereogeometric properties, a careful comparison between PdCl<sub>2</sub>(dppf) and **2** is pertinent. The coordination sphere of the latter is sterically more favored because of the smaller donor atoms (N) and the absence of the diphenyl in proximity.

The sp<sup>2</sup> characteristic of the N donor also minimizes the interference of its substituents on the Pd(II) sphere. This, coupling with the weaker *trans*-influence of the imine compared to phosphine resulted in the significantly shorter, and presumably stronger, Pd–Cl bonds (2.284(4), 2.291(3) Å) compared to those in PdCl<sub>2</sub>(dppf) (2.333(4) and 2.350(9) Å) [9].

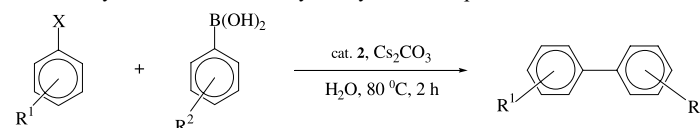
Complex **2** is a highly active catalyst in the Suzuki cross-coupling of aryl iodides and bromides with aryl boronic acids (Table 2). For example, in a suspension of **2** (2 mol%) in aqueous Cs<sub>2</sub>CO<sub>3</sub> (2.8 equivalents) 4-bromobenzonitrile couples with phenyl boronic acid gives near-quantitative yield of 4-phenylbenzonitrile at 80 °C after 2 h (Entry 1). Not surprisingly, the product yield depends on the para-substituents of the aryl halides. Activated, electron-poor aryl halides react near-quantitatively (Entry 1, 2, 3, 6 and 7) whereas deactivated, electron-rich ones give only moderate yields (Entry 4 and 5).

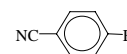
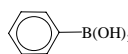
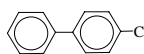
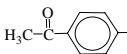
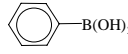
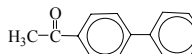
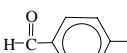
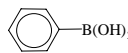
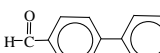
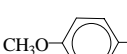
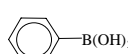
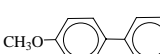
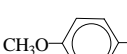
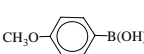
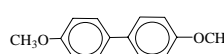
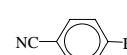
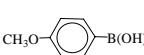
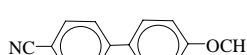
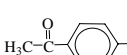
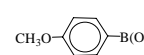
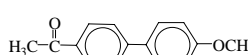
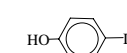
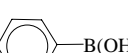
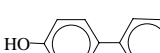
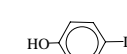
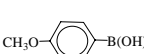
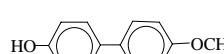
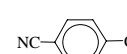
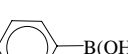
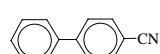
Complex **2** is effective towards both aryl iodides and bromides under similar operational conditions, but inactive towards aryl chlorides (Entry 10). This activity is comparable with PdCl<sub>2</sub>(dppf) which effectively catalyzes the reaction between 4-bromoacetophenone and phenyl boronic acid in toluene at 70 °C giving 94% yield [10]. Catalyst **2** is fairly easy to prepare and with an excellent shelf-life. Its high stability towards oxygen and water and adaptability in aqueous media without the need to achieve full homogeneity are additional advantages.

## 2.2. Effect of the base on coupling between 4-bromoacetophenone and phenylboronic acid

The coupling between 4-bromoacetophenone and phenylboronic acid illustrates the importance of the base, and the choice of it, on the catalytic activity in terms of yield (Table 3). It is generally accepted that the basic nucleophile would assist the departure of halide on Pd(II), thus facilitating the subsequent transmetalation with the boron substrate. Nolan et al. [11] recently demonstrated the highly effective use of Cs<sub>2</sub>CO<sub>3</sub> in a palladium/imidazolium salt system in Suzuki catalyzed reactions. Unfortunately, the more common and less expensive inorganic bases, such as Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>

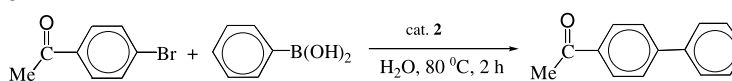
Table 2

Suzuki cross-coupling of aryl halides with aryl boronic acids catalyzed by **2** in an aqueous medium


Entry	Aryl halide	Aryl boronic acid	Product	Isolated yield <sup>a</sup>
1				95
2				94
3				93
4				67
5				51
6				94
7				92
8				95
9				94
10				0

<sup>a</sup> Reaction duration generally not optimized.

Table 3

Effect of the base on the coupling reaction<sup>a</sup>


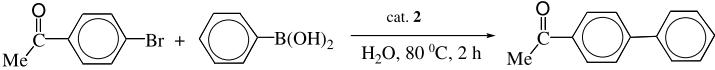
Entry	Base	Yield (%)
1	CS <sub>2</sub> CO <sub>3</sub>	94
2	K <sub>2</sub> CO <sub>3</sub>	96
3	Na <sub>2</sub> CO <sub>3</sub>	98
4	NEt <sub>3</sub>	93
5	KOH	67
6	NaOH	50
7	KF	22

<sup>a</sup> Reaction conditions: 0.5 mmol of 4-bromoacetophenone, 0.67 mmol of phenylboronic acid, 1.4 mmol of base, 0.01 mmol of complex **2**, 5 ml of water, 80 °C, 2 h.

or an organic base, Et<sub>3</sub>N, are less effective. In our case, such differentiation is less obvious whereas all these could lead to higher yields. The basic strength is not a

gauge of the catalytic yield, as illustrated by the lower yields from the use of strong bases KOH or NaOH. This could be understood in terms of their high nucleophilic

Table 4  
Influence of low catalyst loading on the coupling reaction<sup>a</sup>



Entry	Cat <b>2</b> (mol%)	Yield (%)
1	2	94
2	1	94
3	0.5	88
4	0.25	87
5	0.05	47
6	0	<5

<sup>a</sup> Reaction conditions: 0.5 mmol of 4-bromoacetophenone, 0.67 mmol of phenylboronic acid, 1.4 mmol of Cs<sub>2</sub>CO<sub>3</sub>, 5 ml of water, 80 °C, 2 h (for entry 5, 1 h).

effect which could impede the transmetallation process. Accordingly, although KF is one of common and effective bases for Pd<sub>2</sub>(dba)<sub>3</sub>/phosphine Suzuki-type catalytic reaction [12], it is not effective in our case presumably because the strength of the Pd–F bond.

### 2.3. Catalytic load

It is important to achieve good yields using minimum catalysts, particularly so for the use of **2**, as opposed to commercially available reagents such as Pd(OAc)<sub>2</sub>/PR<sub>3</sub>. We therefore examined the effect of catalyst loading on a convenient coupling between 4-bromoacetophenone and phenylboronic acid (Table 4). We have observed high yields (>85%) even at catalyst loadings as low as 0.25 mol%. These are indications of an effective catalytic system that has commercial potential. Further reduction to loads to, for example, 0.05 mol% would result in a moderate yield of 47% and a TON of 940, this is the lower limit of the use of **2** in these reactions. Absence of catalyst generally leads to negligible yields.

### 2.4. Recoverability, reusability and recyclability

An advantage of this method is its simple experimental procedure and the ease of product isolation. Addition of Et<sub>2</sub>O/H<sub>2</sub>O mixture to the mixture at the conclusion of the reaction easily leads to product separation under the biphasic conditions. The organic product could be conveniently isolated from Et<sub>2</sub>O, analyzed by GC/MS and purified by chromatography. Our approach complements some literature examples in Suzuki cross-coupling in aqueous media, which are mainly on the development of water-soluble phosphine ligands [3,13], and use of water as a co-solvent in biphasic reactions [13]. There is also a heterogeneous example in the use of Pd/C as a reusable catalyst for Suzuki reaction of iodophenols in aqueous K<sub>2</sub>CO<sub>3</sub> solution, which also offers a simple high-yield method applicable to water-soluble iodophenols with phenyl boronic acids. However, the yield is significantly lower when bromophenol is used [14].

Other special methods include the use of a ligand-free microwave-mediation in water [15]. It gains from low catalyst loadings and rapid reaction times but is disadvantaged by the use of strenuous conditions (150–175 °C and under pressure). Other “ligandless” approach [using Pd(OAc)<sub>2</sub>] is also efficient in water, but only in the presence of Bu<sub>4</sub>NBr [16]. This however is limited by generally poor conversions for aryl iodides.

Complex **2** was retrieved and recovered from the mixture, verified by <sup>1</sup>H NMR and tested on the 4-bromoacetophenone and phenylboronic acid for its activity (Table 5). The reusable ability of the catalyst is valuable especially in the current case when the catalyst can be conveniently retrieved and reused at the end of a catalytic run. The yields remain good (>85%) after four runs (including original). Even for the fourth and fifth batches, the yields remain at >80%. These are indications that the present catalyst has potential for commercial developments at minimum cost with reasonable effectiveness in terms of yields.

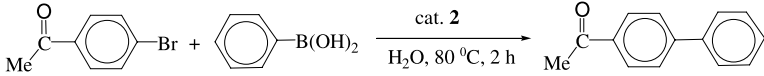
For comparison, we carried out the coupling between 4-bromoacetophenone couple and phenylboronic acid using commercial Pd/C reagent (10 wt%, from Aldrich), which gave unattractive yield (36%). This finding supports that colloidal palladium does not play a key role in this reaction. Similar experiments using **1**/Pd(OAc)<sub>2</sub>, however resulted in good yield (90%). This is consistent with the supporting role of 1,1'-N-substituted ferrocenediyl Fe[η-C<sub>5</sub>H<sub>4</sub>NC(H)Ph–N]<sub>2</sub> (**1**) in promoting high efficiency.

### 2.5. Mechanistic considerations

It has been well established that the general catalytic cycle for the coupling reaction of organoboron reagents with aryl halides involves an oxidative-addition of the aryl halide, transmetalation and reductive-elimination steps (Scheme 2) [1].

Attempts to isolate the intermediate Pd(0) species has not been successful. This is perhaps not surprising in view of its instability and high reactivity. Reaction be-

Table 5  
Recyclability of **2** on the coupling reaction<sup>a</sup>



	Yield (%)
Original use	94
First reuse	93
Second reuse	93
Third reuse	86
Fourth reuse	84
Fifth reuse	83

<sup>a</sup> Reaction conditions: 0.5 mmol of 4-bromoacetophenone, 0.67 mmol of phenylboronic acid, 1.4 mmol of Cs<sub>2</sub>CO<sub>3</sub>, 5 ml of water, 80 °C, 2 h.

tween **2** and K<sub>2</sub>CO<sub>3</sub> in MeOH at r.t. only resulted in 1,1'-*N*-substituted ferrocenediyl (**1**) and a black insoluble precipitate, presumably metallic Pd. The use of a CO reaction atmosphere helped to prevent decomposition to Pd metal but could not yield any isolable species. Attempts to isolate the oxidative addition product from a mixture of **2** with aryl halide and K<sub>2</sub>CO<sub>3</sub> or Cs<sub>2</sub>CO<sub>3</sub> in MeOH at 80 °C resulted in a fairly stable complex (with **1** and other decomposition products), which is presently unidentified.

Our focus is not to study the mechanistic details, which have been reported elsewhere, but we would continue to try to isolate intermediates that are mechanistically significant. The strength of Pd–Cl bonds (in **2**) does not appear to impede the catalytic function. This is attributed to the assistance from the base, which fosters the formation of the key intermediate moiety [Ar–Pd–base]. We are particularly interested to examine if the imine benzaldehyde pendant, through electron donation from the C=N or phenyl functionalities, can protect and hence stabilize the unsaturation sites of the catalytically active species. Work is also underway to expand the scope of *N*-derivatized ferrocenediyl catalysis.

### 3. Experimental

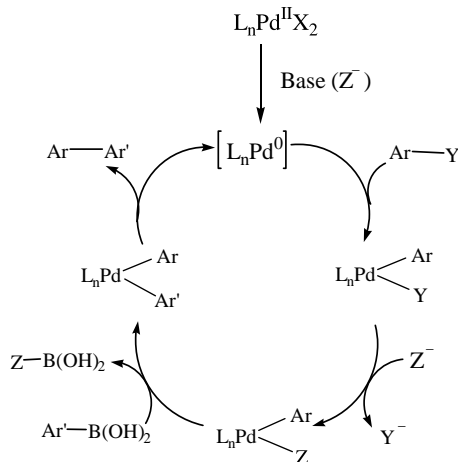
Conventional Schlenk techniques were used unless otherwise indicated. NMR spectra were measured on Bruker ACF300 300 MHz FT NMR spectrometers (<sup>1</sup>H at 300.14 MHz). Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were performed by the microanalytical laboratory in-house. Complex **1** was prepared according to literature procedures [8].

#### 3.1. Synthesis of **2**

To a red solution of **1** (118 mg, 0.3 mmol) in MeOH (8 ml) was added PdCl<sub>2</sub>(MeCN)<sub>2</sub> (78 mg, 0.3 mmol), the red mixture was stirred at r.t. for 24 h. The resultant dark red precipitate was isolated by filtration, washed by toluene and Et<sub>2</sub>O, and dried in vacuo to afford dark-red solid of **2** (143 mg, 0.25 mmol, 84% yield). Anal. Found: C, 49.9; H, 3.4; N, 4.8. Calc. for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>Cl<sub>2</sub>FePd: C, 50.6; H, 3.5; N, 4.9%. <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 6.46 (1H, t, C<sub>5</sub>H<sub>4</sub>), 4.83 (1H, t, C<sub>5</sub>H<sub>4</sub>), 4.62 (1H, t, C<sub>5</sub>H<sub>4</sub>), 4.29 (1H, t, C<sub>5</sub>H<sub>4</sub>), 8.02 (1H, s, CH), 8.65 (2H, d, Ph), 7.49 (1H, t, Ph), 7.36 (2H, t, Ph). FAB-MS (+ve): *m/z*: 569 [M]<sup>+</sup>, 392 [M–2Cl]<sup>+</sup>.

#### 3.2. General procedure for the coupling reactions

Complex **2** (5.6 mg, 0.01 mmol), aryl halide (0.5 mmol), and aryl boronic acid (0.67 mmol) were introduced to a flask under air. The flask was evacuated and refilled with nitrogen. Water (5 ml) was added by syringe, followed by Cs<sub>2</sub>CO<sub>3</sub> (1.4 mmol). The mixture was stirred at 80 °C for 2 h, under ambient pressure of N<sub>2</sub>. The resultant mixture was diluted with H<sub>2</sub>O (10 ml) and ether (10 ml), and the aqueous layer extracted twice by Et<sub>2</sub>O. The ethereal extract was stripped of solvent under vacuum and the products purified by column chromatography on silica. The residual catalyst, which is insoluble in both ether and water, distributed on the wall of the separatory funnel, could be collected and reused (simply as a suspension in water).



Scheme 2.

Table 6  
Selected crystal data, data collection and refinement parameters for compound **2**

Formula	C <sub>24</sub> H <sub>20</sub> Cl <sub>2</sub> FeN <sub>2</sub> Pd·CH <sub>2</sub> Cl <sub>2</sub>
Formula weight	654.50
Color, habit	Dark red block
Crystal size (mm)	0.16 × 0.06 × 0.04
Temperature (K)	223(2)
Crystal system	P2(1)/c
Space group	Monoclinic
<i>a</i> (Å)	14.6596(19)
<i>b</i> (Å)	16.554(2)
<i>c</i> (Å)	19.643(2)
$\alpha$ (°)	90
$\beta$ (°)	92.744(5)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	4761.2(10)
<i>Z</i>	8
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.826
Radiation used	Mo K $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.832
$\theta$ range (°)	1.86 to 22.50
No. of unique reflections measured	21,559
Max., min. transmission	0.9303, 0.7582
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0792, <i>wR</i> <sub>2</sub> = 0.1530
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1381, <i>wR</i> <sub>2</sub> = 0.1756
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.975
Large diff. peak and hole (e Å <sup>-3</sup> )	2.274 and -0.898

### 3.3. Structure determinations

Single-crystals of **2** were obtained by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution of **2** at ambient temperature. A suitable crystal was mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using Mo K $\alpha$  radiation ( $\lambda$  0.71073 Å). The data were corrected for Lorentz and polarisation effects with the SMART suite of programs [17] and for absorption effects with SADABS [18]. Structure solution and refinement were carried out with the SHELXTL suite of programs [19]. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Due to the small crystal size and the small number of reflections, the C atoms are not refined anisotropically. The data collection and processing parameters are given in Table 6.

### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 205748. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44-1223-336033, or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>].

### Acknowledgements

We are grateful to the Agency for Science, Technology & Research (Singapore), the Institute of Chemical and Engineering Sciences (Singapore) (Grant 012-101-0035) and the National University of Singapore for support.

### References

- [1] (a) A. Suzuki, *J. Organomet. Chem.* 576 (1999) 147 (and references therein);  
(b) J. Yin, M.P. Rainka, X.-X. Zhang, S.L. Buchwald, *J. Am. Chem. Soc.* 124 (2002) 1162;  
(c) R.B. Bedford, C.S.J. Cazin, *Organometallics* 22 (2003) 987.
- [2] Q. Cheng, N. Valmas, P.E.B. Reilly, P.J. Collins, R. Kopittke, P.R. Ebert, *Toxicol. Sci.* 73 (2003) 60.
- [3] J.P. Genet, M. Savignac, *J. Organomet. Chem.* 576 (1999) 305 (and references therein).
- [4] (a) A.L.C. Tan, P.M.N. Low, Z.Y. Zhou, W. Zheng, B.M. Wu, T.C.W. Mak, T.S.A. Hor, *J. Chem. Soc., Dalton Trans.* (1996) 2207;  
(b) P.M.N. Low, A.L.C. Tan, T.S.A. Hor, Y.-S. Wen, L.-K. Liu, *Organometallics* 15 (1996) 2595;  
(c) L. Lassova, H.K. Lee, T.S.A. Hor, *J. Org. Chem.* 63 (1998) 3538;  
(d) X.-L. Xu, S.W.A. Fong, Z.-H. Li, Z.-H. Loh, F. Zhao, J.J. Vittal, W. Henderson, S.B. Khoo, T.S.A. Hor, *Inorg. Chem.* 41 (2002) 6838.
- [5] (a) K.-S. Gan, T.S.A. Hor, in: A. Togni, T. Hayashi (Eds.), *Ferrocenes-Homogeneous Catalysis, Organic Synthesis, Materials Science*, VCH, Weinheim, 1995, p. p3;  
(b) G. Bandoli, A. Dolmella, *Coord. Chem. Rev.* 209 (2002) 161.
- [6] (a) J.M. Brown, N.A. Cooley, *J. Chem. Soc., Chem. Commun.* (1988) 1345;

- (b) T. Ohe, N. Miyaura, A. Suzuki, *J. Org. Chem.* 58 (1993) 2201;  
(c) O.R. Hughes, J.D. Unruh, *J. Mol. Catal.* 12 (1981) 71.
- [7] A. Shafir, M.P. Power, G.D. Whitener, J. Arnold, *Organometallics* 19 (2000) 3978.
- [8] (a) V.C. Gibson, N.J. Long, E.L. Marshall, P.J. Oxford, A.J.P. White, D.J. Williams, *J. Chem. Soc., Dalton Trans.* (2001) 1162;  
(b) V.C. Gibson, C.M. Halliwell, N.J. Long, P.J. Oxford, A.M. Smith, A.J.P. White, D.J. Williams, *J. Chem. Soc., Dalton Trans.* (2003) 918.
- [9] G.M. De Lima, C.A.L. Filgueiras, M.T.S. Giotto, Y.P. Mascarenhas, *Trans. Met. Chem.* 20 (1995) 380.
- [10] T.J. Colacot, H. Qian, R. Cea-Olivares, S. Hernandez-Ortega, *J. Organomet. Chem.* 637–639 (2001) 691.
- [11] G.A. Grasa, M.S. Viciu, J. Huang, C. Zhang, M.L. Trudell, S.P. Nolan, *Organometallics* 21 (2002) 2866.
- [12] (a) A.F. Littke, C. Dai, G.C. Fu, *J. Am. Chem. Soc.* 122 (2000) 4020, and references therein;  
(b) M.R. Pramick, S.M. Rosemeier, M.T. Beranek, S.B. Nickse, J.J. Stone, R.A. Stockland Jr., S.M. Baldwin, M.E. Kastner, *Organometallics* 22 (2003) 523.
- [13] K.H. Shaughnessy, R.S. Booth, *Org. Lett.* 3 (2001) 2757 (and references therein).
- [14] H. Sakurai, T. Tsukuda, T. Hirao, *J. Org. Chem.* 67 (2002) 2721.
- [15] N.E. Leadbeater, M. Marco, *Org. Lett.* 4 (2002) 2973.
- [16] D. Badone, M. Baroni, R. Cardamone, A. Ielmini, U. Guzzi, *J. Org. Chem.* 62 (1997) 7170.
- [17] SMART version 5.1, Bruker Analytical X-ray Systems, Madison, WI, 2000.
- [18] Sheldrick, G.M. SADABS, A program for Empirical Absorption Correction, Göttingen, Germany, 2000.
- [19] SHELXTL version 5.03, Bruker Analytical X-ray Systems, Madison, WI, 1997.