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Tetrahedron
Tetrahedron 63 (2007) 4625–4629

Cyclopalladated ferrocenylimine: a highly effective catalyst for the borylation/suzuki coupling reaction

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Received 23 January 2007; revised 15 March 2007; accepted 19 March 2007
Available online 21 March 2007

Abstract—The cyclopalladated ferrocenylimine was an efficient catalyst for the borylation/Suzuki coupling reaction. The catalytic loading for the reaction containing bromoarenes was 1 mol %. When iodobenzene was used, the catalytic loading was as low as 0.1 mol %. Furthermore, the cyclopalladated ferrocenylimine also exhibited excellent catalytic power in the case of substrates containing electron-donating substituents, with yields reaching 93% or higher.

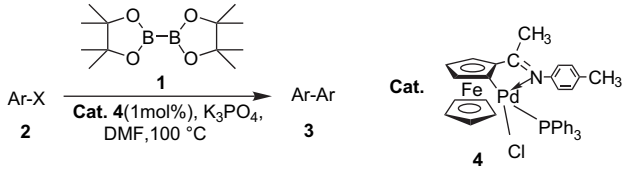
1. Introduction

Substituted biaryls are an important class of versatile intermediates, which have been widely used in the total synthesis of natural products and pharmaceuticals.[1] Suzuki cross-coupling reactions[2] and homocoupling reactions[3] of aryl halides by palladium catalyst are two main approaches that have been used in several studies to synthesize biaryls. The Suzuki cross-coupling method remains a significant challenge because obtaining the boronic acid derivative reactants often requires the use of strong bases such as organolithium compounds[4] and reactions to be carried out under temperatures as low as −78 °C. As to the direct homocoupling approach, high catalytic loading and long reaction time severely limit its practical applications. Recently, a new method, namely one-pot borylation/Suzuki cross-coupling reaction,[5g] has received much attention for its mild reaction conditions. [5] In contrast to other approaches, this latest approach does not require isolation of the arylboronic ester intermediates. However, the reported one-pot approach still requires high catalytic loading. When $PdCl_2$(dppf) (dppf=diphenylphosphinoferrocene) was used as the catalyst, the reaction rates were found to be very slow for the substrates containing electron-donating or bulky substituents.[5e] $PdCl_2$ was noted to undergo quick degradation, yielding black palladium. The reaction rates were markedly increased under microwave reaction condition; yet with catalytic loadings as high as 10 mol %.[5g] Nonetheless, the one-pot borylation/Suzuki cross-coupling reaction remains an important method for the synthesis of biaryls.

In this work, we first investigated the Suzuki cross-coupling reactions using previously reported cyclopalladated ferrocenylimine as the catalyst for the synthesis of symmetrical biaryls in the one-pot borylation fashion.

2. Results and discussion

In order to find a better catalyst for the synthesis of symmetrical biaryls, we tested the cyclopalladated ferrocenylimine **4**, which was first synthesized in our laboratory,[6] in catalyzing biaryl synthesis in the one-pot fashion reported by Nising et al.[5e] and also shown in Scheme 1.



Scheme 1. Synthesis of symmetrical biaryls.

We first tested cyclopalladated ferrocenylimine **4** as the catalyst under the reaction conditions fashioned by Ishiyama et al.[7] These investigators reported that K_3PO_4 or K_2CO_3, and polar solvent (DMSO or DMF) displayed a promoting effect on the transformation of symmetrical biaryls from corresponding aryl halides. As shown in Table 1, we found that using DMF as the solvent and K_3PO_4 as the base at

Keywords: Cyclopalladated ferrocenylimine; Bis(pinacolato)diboron; One-pot borylation; Suzuki cross-coupling.
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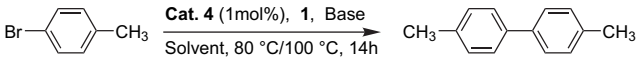
doi:10.1016/j.tet.2007.03.108

Table 1. Optimal reaction conditions[a]



Entry	Conditions			Yields[b] (%)
	Solvent	Base	Temp (°C)	
1	DMSO	K_2CO_3	80	33
2	DMSO	K_3PO_4	80	56
3	DMF	K_2CO_3	80	64
4	DMF	K_3PO_4	80	73
5	DMF	K_3PO_4	100	82
6[c]	DMF	K_3PO_4	100	93

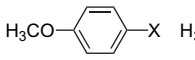
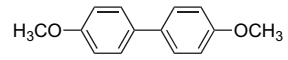
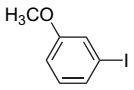
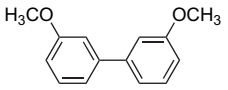
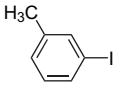
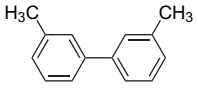
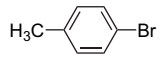
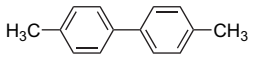
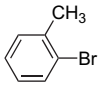
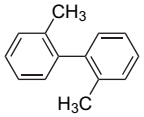
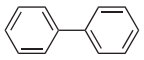
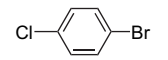
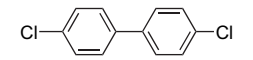
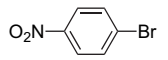
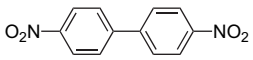
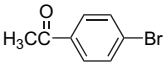
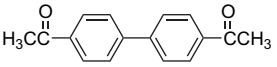
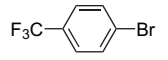
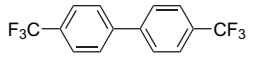
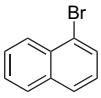
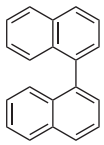
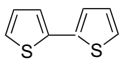
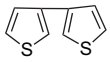
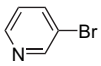
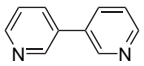
[a] Reaction conditions: 4-bromotoluene (1 equiv), **1** (0.5 equiv), cat. **4** (1 mol %), base (5 equiv), solvent (3 mL), 80 °C or 100 °C, 14 h, under N_2 atmosphere.
[b] Isolated yields.
[c] Addition of PPh_3 (1 mol %).

a temperature of 100 °C and catalytic loading of 1 mol %, reaction yield reached 82% (entry 5), and that incorporation of PPh_3 at a level of 1 mol %, the yield could be improved to 93% (entry 6). These results demonstrated that the cyclopalladated ferrocenylimine **4** is a powerful and efficient catalyst in biaryl synthesis via a one-pot borylation fashion.

We next carried out similar reactions with 18 other substrates containing various substituents (Table 2). As shown in Table 2 from entry 1 to 5, at 1 mol % catalytic loading, reactions with substrates containing electron-donating substituents gave yields ranging from 93% to 98%. Under the same reaction conditions, the yield for *o*-bromotoluene was 68% (entry 6), indicating that the steric hindrance likely has a negative effect on the synthetic reaction of symmetrical biaryls as others have reported.[5e] When iodobenzene substrate was used, a near 100% reaction yield was obtained (entry 7) at a 1 mol % catalytic loading. Interestingly, even at a catalytic loading as low as 0.1%, the yield was still as high as 94% (entry 8). The yields for the reactions with substrates containing electron-withdrawing and bulky substituents were ranging from 63% to 89% (from entry 11 to 15). The yields for the heterocyclic substrates were good to excellent, ranging from 78% to 93% (from entry 16 to 18). The data showed that the cyclopalladated ferrocenylimine **4** can be used to catalyze the synthesis of a variety of biaryls with good to excellent yields at low catalytic loadings.

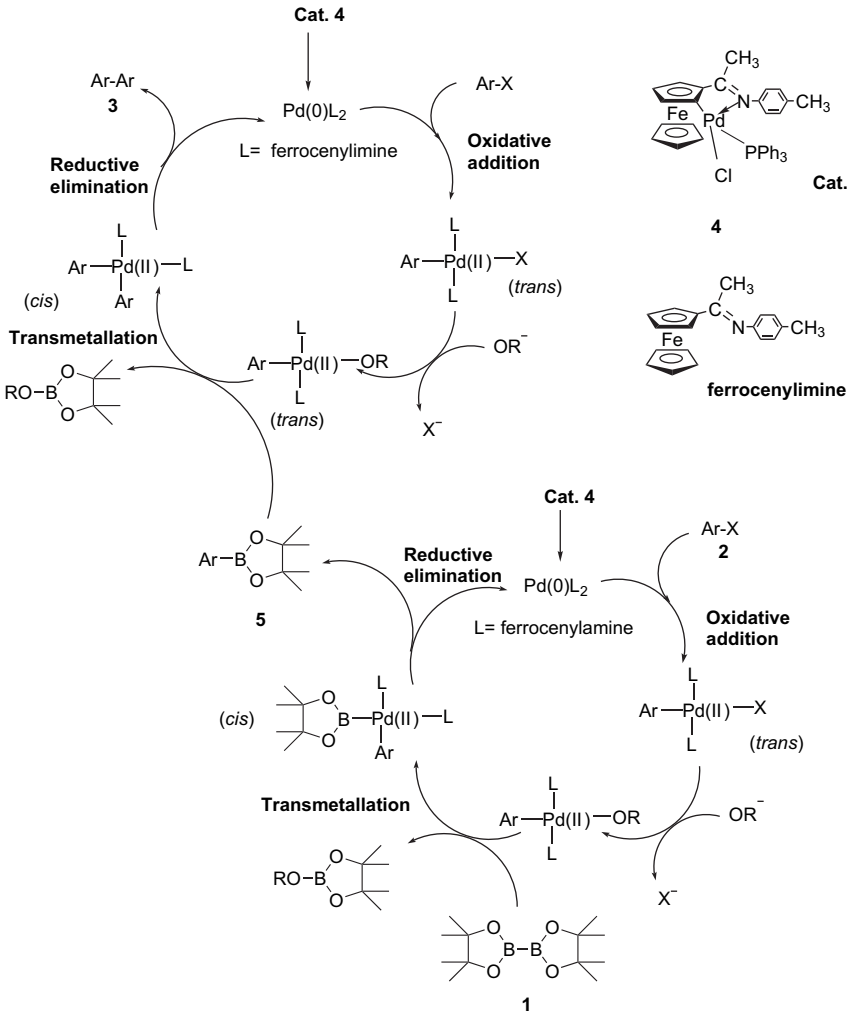
We have investigated the Suzuki cross-coupling reactions in a one-pot borylation fashion using cyclopalladated ferrocenylimine **4**[6] as the catalyst. The current work reports a significantly improved system for biaryl synthesis via Suzuki cross-coupling reactions. Other investigators have also fashioned the original Suzuki cross-coupling reactions to improve its application in biaryl synthesis. A one-pot borylation approach was developed to avoid isolation of arylboronic ester intermediates. In comparison to previously reported methods, using current approach of cyclopalladated ferrocenylimine catalyzing Suzuki cross-coupling reactions has an advantage of low catalytic loading, with high reaction yields. We have shown that using our system, the catalytic loading with iodobenzene substrates could be lowered to 0.1 mol % with reaction yield approximately 100%. The data reported in this work shows that cyclopalladated ferrocenylimine **4** can be used as a powerful and efficient catalyst to synthesize biaryls by a one-pot borylation fashion.

Table 2. Synthesis[a] of symmetrical biaryls from haloarenes (Scheme 1)

Entry	Aryl Halide **2**	Product **3**	Yield[b] (%)
			
1	X=I		98
2[c]	X=Br		95
3			97
4			95
5[c]			93
6[c]			68
			
7	X=I		>99
8[d]	X=I		94
9	X=Br		90
10	X=Cl		20
11			78
12			85
13			63
14			86
15			89
16[c]			93
17[c]			78
18[c]			88

[a] Reaction conditions: haloarene (1 equiv), **1** (0.5 equiv), cat. **4** (1 mol %), base (5 equiv), solvent (3 mL), 100 °C, 14 h, under N_2 atmosphere.
[b] Isolated yields.
[c] Addition of PPh_3 (1 mol %).
[d] Catalyst loading was reduced to 1 mol %.

Regarding the coupling reaction mechanism, it is generally believed to consist of two parts (Scheme 2),[1f,2a,2l,5e,7,8] which both contain three main steps: oxidative addition,



Scheme 2. Proposed reaction mechanism for the formation of the biaryls.

transmetallation, and reductive elimination. In the first part, under higher reaction temperature, the Pd–C bond in cyclopalladated ferrocenylimine **4** undergoes rupture, thereby generating Pd(0) species. It has been believed that the real catalytic species is Pd(0), rather than the Pd(II). The rupture of the Pd–C bond also releases ferrocenylimine. We propose that the ferrocenylimine in turn coordinates the Pd(0) forming $Pd(0)L_2$, therefore stabilizing the Pd(0) catalytic core. The stabilization of the catalytic core by the ferrocenylimine may explain the low catalytic loadings and high reaction yields that we observed and reported in this work. The $Pd(0)L_2$ reacts with haloarene **2** through an oxidative addition mechanism, which results in the formation of the corresponding pentacoordinated palladium(II) species.

As depicted in the second part of the proposed mechanism, the ferrocenylimine-coordinated Pd(0) catalytic species also catalyzes similar oxidative addition, transmetallation, and reductive elimination reactions, leading to the formation of arylboronic esters **5**. We propose that the arylboronic ester **5** reacts with the ferrocenylimine-containing pentacoordinate palladium(II) catalytic intermediate species (formed in the first part of the proposed mechanism), generating the *cis*-$Pd(II)Ar_2L_2$ intermediate. Subsequently, this intermediate undergoes reductive elimination reaction resulting in the synthesis of biaryls **3**, therefore, completing a full catalytic cycle.

As described above, the observed high catalytic power of cyclopalladated ferrocenylimine in catalyzing the synthesis of biaryls may be due to stabilization of the catalytic core Pd(0) by ferrocenylimine coordination. This assertion is supported by others and our observation of the effect of PPh_3 on Pd(0) catalysis. The electron-rich aryl bromides and heterocyclic bromides are less active substrates. These types of substrates often give low biaryl yields of the one-pot borylation/Suzuki cross-coupling reactions. However, we found that when PPh_3 was added, the biaryl yields were as high as those of the reactive substrates (Table 2 entries 2, 5, 6, and 16–18), with low catalytic loadings. Other investigators have also reported similar PPh_3 effects and interpreted that the presence of PPh_3 facilitated the oxidative addition to C–Br bond and protected active palladium center from deactivation in the catalytic cycle. We suspect that the PPh_3 acted by coordinating Pd(0), therefore further stabilizing the ferrocenylimine-containing Pd(0) catalytic core. As a consequence, it remains catalytically active. In conclusion, cyclopalladated ferrocenylimine displayed a high catalytic power in biaryl synthesis via a one-pot borylation/Suzuki cross-coupling reaction. Our data indicated

that stabilizing catalytic Pd(0) core through coordination such as by ferrocenylimine and PPh_3 ligands might represent a viable approach to fine-tune the catalysis for biaryls synthesis via the one-pot borylation/Suzuki cross-coupling reactions.

3. Conclusion

In summary, the above data showed that the cyclopalladated ferrocenylimine **4** was a highly efficient catalyst for the synthesis of symmetrical biaryls via one-pot borylation/Suzuki cross-couplings. This was likely because ferrocenylimine stabilized catalytic core by coordinating Pd(0).

4. Experimental

4.1. Reagents

The catalyst **4** (cyclopalladated ferrocenylimine) was synthesized following the reported procedures.[6] Commercially available reagents and DMF were used without further purification. All reactions were performed under nitrogen. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$/DMSO-d_6 as the solvent and TMS as an internal standard. All products were purified and identified by ^1H NMR and ^{13}C NMR spectra analysis.

4.2. General procedure for the one-pot borylation/Suzuki cross-coupling of haloarenes (Table 2)

A mixture containing 1 mmol of the corresponding haloarene (Table 2), 7.2 mg (0.01 mmol, 1 mol %) of cyclopalladated ferrocenylimine, 2.6 mg (0.01 mmol, 1 mol %) of PPh_3, 127 mg (0.5 mmol, 0.5 equiv) of bis(pinacolato)diboron, and 1060 mg (5 mmol, 5 equiv) of finely crushed K_3PO_4 powder (analytical grade) was suspended in 3 mL of DMF. The mixture was stirred under nitrogen atmosphere at 100 °C for 14 h. After cooling to room temperature, water and ethyl acetate were added. The organic phase was washed with water and dried over Na_2SO_4. The solvent was evaporated under vacuum. The biaryl product was purified by preparative thin layer chromatography.

4.2.1. 4,4′-Dimethoxy-biphenyl (entries 1 and 2).[5e] White solid; mp 175–176 °C (lit=175 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.47 (d, J=8.6 Hz, 4H), 6.95 (d, J=8.6 Hz, 4H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 133.5, 127.7, 114.2, 55.4.

4.2.2. 3,3′-Dimethoxy-biphenyl (entry 3).[3d] White solid; mp 36–37 °C (lit=36 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.35 (t, J=7.9 Hz, 2H), 7.18 (d, J=7.7 Hz, 2H), 7.12 (t, J=3.8 Hz, 2H), 6.90 (dd, J=8.2, 2.2 Hz, 2H), 3.86 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 142.6, 129.7, 119.7, 113.0, 112.8, 55.3.

4.2.3. 3,3′-Dimethyl-biphenyl (entry 4).[9,10] Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.45 (d, J=8.0 Hz, 4H), 7.37 (t, J=7.4 Hz, 2H), 7.20 (d, J=7.4 Hz, 2H), 2.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 138.3, 128.1, 124.4, 21.6.

4.2.4. 4,4′-Dimethyl-biphenyl (entry 5).[5e] White solid; mp 122–123 °C (lit=122–123 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.66 (d, J=8.0 Hz, 4H), 7.41 (d, J=8.0 Hz, 4H), 2.56 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 136.3, 129.4, 126.8, 21.2.

4.2.5. 2,2′-Dimethyl-biphenyl (entry 6).[3i] Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.26–7.20 (m, 6H), 7.11 (d, J=6.9 Hz, 2H), 2.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 135.8, 129.8, 129.3, 127.2, 125.5, 19.8.

4.2.6. Biphenyl (entries 7–10).[5e] White solid; mp 67–69 °C (lit=68 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.60 (d, J=7.5 Hz, 4H), 7.44 (t, J=7.2 Hz, 4H), 7.35 (t, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 129.8, 127.3, 127.1.

4.2.7. 4,4′-Dichloro-biphenyl (entry 11).[3m,10] Colorless solid; mp 147 °C (lit=147–149 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.45 (d, 4H, J=10.8 Hz), 7.40 (d, 4H, J=10.8 Hz); ^{13}C NMR (100 MHz, DMSO): δ 138.5, 133.8, 129.1, 128.3.

4.2.8. 4,4′-Dinitro-biphenyl (entry 12).[5e] Brown solid; mp 238 °C (lit=240 °C); ^1H NMR (400 MHz, DMSO, TMS): δ 8.36 (d, J=8.8 Hz, 4H), 8.09 (d, J=8.8 Hz, 4H); ^{13}C NMR (100 MHz, DMSO): δ 147.8, 144.3, 128.9, 124.4.

4.2.9. 4,4′-Diacetyl-biphenyl (entry 13).[5e] Colorless solid; mp 191–192 °C (lit=193–194 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.07 (d, J=8.4 Hz, 4H), 7.72 (d, J=8.4 Hz, 4H), 2.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 144.3, 136.6, 129.0, 127.4, 26.7.

4.2.10. 4,4′-Bis-ditrifluoromethyl-biphenyl (entry 14).[3i] White solid; mp 82–83 °C (lit=83–84 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.69–7.75 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 133.6, 127.5, 114.4, 55.5.

4.2.11. 1,1′-Binaphthyl (entry 15).[5e] White solid; mp 154–156 °C (lit=155–156 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.95 (d, J=8.2 Hz, 2H), 7.94 (d, J=8.0 Hz, 2H), 7.59 (t, J=8.0 Hz, 2H), 7.50–7.47 (m, 4H), 7.38 (d, J=8.3 Hz, 2H), 7.28 (t, J=7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 133.5, 132.8, 128.1, 127.9, 127.8, 126.6, 126.0, 125.8, 125.3.

4.2.12. 2,2′-Bithiophene (entry 16).[5e] White solid; mp 31 °C (lit=30–32 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (d, J=4.8 Hz, 2H), 7.17 (d, J=3.6 Hz, 2H), 7.00–7.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 127.8, 124.4, 123.8.

4.2.13. 3,3′-Bithiophene (entry 17).[3m,11] Colorless solid; mp 130 °C (lit=130–131 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.37 (d, J=1.4 Hz, 2H), 7.33–7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 126.4, 126.1, 119.8.

4.2.14. 3,3′-Bipyridine (entry 18).[3m,10] Yellow oil; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.85 (s, 2H), 8.66 (t, J=3.3 Hz, 2H), 7.92–7.89 (m, 2H), 7.45–7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 148.1, 134.6, 133.5, 123.9.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (Project 20472074) and the Innovation Found for Outstanding Scholar of Henan Province (Project 0621001100) for the financial support given to this research. We thank Mr. Jeffrey Misiaszek and Dr. Yusheng Wu for valuable discussion of this paper.

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