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Bis(diphosphaferrocene) palladium(II) dimer complexes as efficient catalysts in the synthesis of arylboronic esters

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Abstract

Bis(diphosphaferrocenes)PdCl$_2$ dimers efficiently catalyse cross-coupling reactions between aryl iodides and pinacol borane in dioxane at 80 °C to afford the corresponding aryl boronic esters derivatives in excellent yields. © 2001 Elsevier Science B.V. All rights reserved.

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Aryl boronic esters and acids are very useful synthons in many organic transformations [1]. It has also been found that they have interesting applications in biology [2] and for the elaboration of electron transfer sensors [3]. In organic chemistry, their importance has been emphasized by the palladium-catalysed Suzuki cross-coupling reaction, which allows the synthesis of functionalised biphenyl derivatives [4]. Classical synthetic approaches towards these boronic esters hinge on transmetallation reactions between organomagnesium or lithium derivatives with boron compounds [5]. However, the direct Pd-catalysed cross-coupling reaction involving the condensation of either tetraalkoxydiboranes or dialkoxyhydroboranes with halogenoarenes proved to be an interesting alternative [6]. This simple synthetic sequence, known as the Miyaura coupling, requires relatively large amounts of catalyst (typically about 1–5 mol%) and improvements aimed at reducing the load of catalyst are clearly needed to render this procedure very attractive. In the course of a study dealing with the use of diphosphaferrocenes [7] as ligands in homogeneous catalysis [8], we recently showed that the easily available bis(octaethyldiphosphaferrocene) palladium(0) complex **1** could efficiently catalyse the Suzuki cross-coupling reaction between phenylboronic acid and various bromoarenes (TON up to 1.10^6) [9]. This result prompted us to explore the catalytic activity of this new class of complexes in the Miyaura coupling. A first series of experiments carried out with several aryl iodides and pinacol borane as reactants using the palladium(0) complex **1** as catalyst (0.1 mol%) only showed a slight improvement. Thus (phenyl)pinacolboronic ester was obtained in a 75% yield after 60 h of heating in dioxane using triethylamine as base. Considering that in this type of coupling, [Pd(L$_2$)Cl$_2$] (L$_2$ = chelate ligand) complexes often yield better results than homoleptic [PdL$_4$] (L = monophosphine) species, we next focused our work on the use of the diphosphaferrocene palladium(II) complexes such as **2** which is conventionally prepared by reacting equimolar amounts of the (ocatethyl)-diphosphaferrocene with the [Pd(COD)Cl$_2$]. These complexes were shown not to exist as monomers but as dimers mainly for structural reasons [10] (Chart 1).

In a first run, a significant improvement was obtained with only 0.05 mol% of catalyst **2** leading to a quantitative conversion. Interestingly, we found that three consecutive batches could be carried out with no significant loss in product yields and TOF. The synthesis of (2-furanyl)pinacolboronic ester derivative is representative. Thus, 2-iodofurane (1.6 mmol), pinacolborane (2.4 mmol) and Et$_3$N (4.8 mmol) were successively added at 25 °C to a mixture of catalyst **2** (0.05 mol%) in dioxane (10 ml) and the resulting mixture was heated at 80 °C. After 48 h of heating, pinacolborane, 2-iodofurane and

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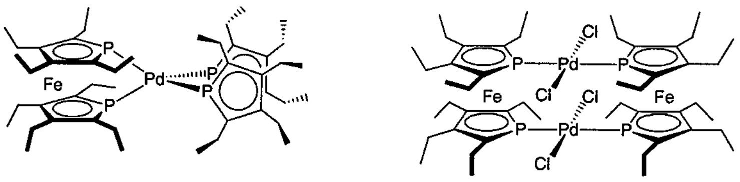
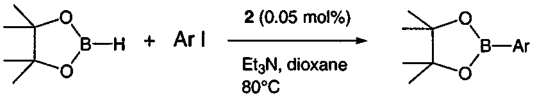


1 **2**

Chart 1.

Et_3N were reloaded and heating was pursued for 48 h. After a second reload using the same amount of reactants and solvent, an extraction with ether followed by a flash chromatography afforded the functionalised furane as a brownish oil in an overall 86% yield (Eq. (1)).



(1)

Whereas it would appear that this coupling is relatively insensitive to steric effects (see Table 1 entries 5 and 6), the nature of the halogen plays a significant role. Thus, no coupling was observed with aryl bromides. This result is fully rational if we consider that coordination of diphosphaferrocene, which is a relatively strong π-acceptor ligand, decreases electron density at the Pd centre and therefore disfavours the initial oxidative addition step. Additional experiments aimed at identifying the nature of the active species have been unsuccessful so far. However, we can reasonably propose that the dimeric structure of complex **2** is not maintained in solution and that this dimer serves as a precursor of a 12 or 14 electron (octaethyldiphosphaferrocene)Pd(0) complex which is probably the active species. In conclusion, we have showed that the use of dimeric diphosphaferrocene Pd(II) based catalysts improves the Miyaura cross-coupling reaction. Though aryl iodides are usually more expensive than arylbromides, the increased TON (hundred times better than usual catalysts) renders the use of catalyst such as **2** very attractive. Furthermore aryl-pinacolboronic ester derivatives were formed in very good yields. Studies aimed at exploring the catalytic activity of complex such as **2** in other processes of importance are currently underway in our laboratories.

Table 1
Cross-coupling reaction between pinacolborane and various aryl iodides [a]

Entry	Aryl iodide	Yield [b] (%)	TON
1	Iodobenzene	95	2862
2	1-Iodo-4-bromobenzene	94	2839
3	*p*-Iodotoluene	95	2866
4	*p*-Iodoanisole	96	2884
5	*o*-Iodotoluene	98	2966
6	*o*-Iodoanisole	89	2693
7	2-Iodothiophene	96	2901
8	2-Iodofurane	86	2581
9	2-Iodonaphthalene	92	2760

[a] Reactions were carried out utilizing one equivalent of aryl iodide and 1.5 equivalents of pinacolborane with 0.05 mol% catalyst **2** in refluxing dioxane with three equivalents of Et_3N as base.

[b] Isolated yields after three runs.

1. General procedure

All reactions were performed under an inert atmosphere of dry nitrogen by using Schlenk techniques and dry deoxygenated solvents. Pinacolborane (2.4 mmol), iodoaryl (1.6 mmol) and Et_3N (4.8 mmol) were successively added at 25 °C using a syringe to a solution of catalyst **2** (1 mg, 0.8 μmol) in dioxane (10 ml). The resulting mixture was heated in an oil bath at 80 °C and the progress of the reaction was monitored by gas chromatography. After 48 h, no traces of the starting iodoaryl could be detected in the reaction medium. Pinacolborane (2.4 mmol), iodoaryl (1.6 mmol) and Et_3N (4.8 mmol) were added and the mixture was further heated for 48 h. After controlling the disappearance of the starting iodoaryl, the reaction was reloaded. After an additional 48 h heating, the mixture was cooled to room temperature and the mixture was evaporated to dryness. Ether (2 × 10 ml) was added to allow the separation of the $Et_3NH^+ \cdot I^-$ salt and the solution was filtrated. Celite (1 g) was then added and the solvent was evaporated yielding a pale yellow powder, which was deposited onto the top of a silicagel column for chromatography (silicagel was treated with a solution of hexane–Et_3N (95:5) prior to chromatography). The arylboronic esters were eluted with hexane as eluent.

1.1. *4,4,5,5-Tetramethyl-2-phenyl-[1,3,2]dioxaborolane*

Yield: 310 mg (95%). For characterizations, see Ref. [6c].

1.2. 2-(4-Bromo-phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane

Yield: 424 mg (94%). For characterizations, see Ref. [6a].

1.3. 4,4,5,5-Tetramethyl-2-p-tolyl-[1,3,2]dioxaborolane

Yield: 331 mg (95%). For characterizations, see Ref. [6c].

1.4. 2-(4-Methoxy-phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane

Yield: 359 mg (96%). For characterizations, see Ref. [6b].

1.5. 4,4,5,5-Tetramethyl-2-o-tolyl-[1,3,2]dioxaborolane

Yield: 341 mg (98%). For characterizations, see Ref. [6c].

1.6. 2-(2-Methoxy-phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane

Yield: 333 mg (89%). For characterizations, see Ref. [6c].

1.7. 4,4,5,5-Tetramethyl-2-thiophen-2-yl-[1,3,2]-dioxaborolane

Yield: 322 mg (96%). For characterizations, see Ref. [6c].

1.8. 4,4,5,5-Tetramethyl-2-furan-2-yl-[1,3,2]-dioxaborolane

Yield: 267 mg (86%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 12H, Me), 6.42 (dd, 1H, $^3J_{HH} = 1.62$ Hz, $^3J_{HH} = 3.36$ Hz, 4-H), 7.06 (d, 1H, $^3J_{HH} = 3.36$ Hz, 3-H), 7.63 (d, 1H, $^3J_{HH} = 1.62$ Hz, 5-H); ^{13}C-NMR (50.32 MHz, $CDCl_3$) δ 24.5 (s, Me), 83.0 (s, 2-C), 84.0 (s, C–O), 110.2 (s, 4-C), 123.1 (s, 3-C), 147.1 (s, 5-C); EIMS m/z (%): 194 (M^+, 40), 151 (M-43, 100). Anal. Found: C, 62.15; H, 7.83. Calc. for $C_{10}H_{15}BO_3$: C, 61.90; H, 7.79%.

1.9. 4,4,5,5-Tetramethyl-2-naphthalen-2-yl-[1,3,2]-dioxaborolane

Yield: 373 mg (92%). For characterizations, see Ref. [6c].

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