



Palladium-catalyzed Suzuki couplings using a novel diaminophosphine oxide as ligand

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Abstract

A novel diaminophosphine oxide was synthesized and applied as ligand in palladium-catalyzed Suzuki couplings reaction of aryl bromides and chlorides. The coupling reaction proceeded smoothly at mild conditions using 2 mol% Pd₂(dba)₃ in the presence of ^tBuOK.

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Palladium-catalyzed Suzuki reactions are extremely powerful synthetic tools now [1–3]. It is a clear proof that it won the Nobel Prize of Chemistry in 2010 due to its widely application in natural products, industrial intermediates, pharmaceuticals and molecular materials [4–7]. A lot of palladium catalysts efficiently promote Suzuki couplings of aryl halides and other electrophiles with arylboronic acids. In these catalyst systems, ligands such as phosphorus ligands, carbene ligands, nitrogen ligands play important role [8–11]. A wide variety of ligands were developed to promote the efficiency of the transformation, but the study of diaminophosphine oxide as ligand remains rare [12]. Phosphorus ligands, especially electron-rich phosphine ligands are often air-sensitive and therefore require air-free handling to minimize ligand oxidation. Phosphine oxides maybe solve the problem because they are more stable and antioxidative in air.

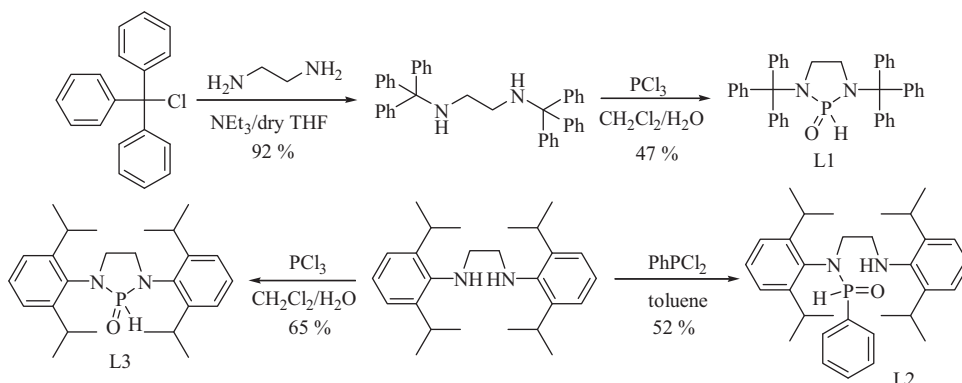
Li first presented an alternative method that use alkyl-substituted secondary phosphine oxide in palladium-catalyzed Suzuki couplings [13]. Ackermann and Boln [12] have reported a diaminophosphine oxide as new and high efficient ligand in Suzuki reaction. This type of ligand has potential value in palladium-catalyzed cross-couplings, but it has received little attention.

1. Results and discussion

Herein we wish to report a new diaminophosphine oxide (L1) (Scheme 1) as novel and efficient ligand for palladium-catalyzed Suzuki cross-couplings of aryl bromides and chlorides with arylboronic acids. As shown in Scheme 1, we synthesized new phosphine oxide compounds L1 and L2 in moderate yields using modified procedure. L3 is known ligand which was reported by Ackermann and Boln [12].

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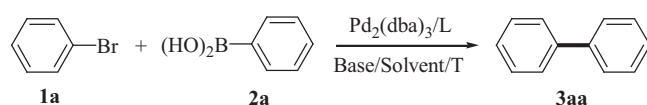


Scheme 1. Synthesis of L1, L2 and L3.

With L1 and L2 in hand, we first tested their catalytic activity with $\text{Pd}_2(\text{dba})_3$ for Suzuki reaction using phenylbromide (**1a**) and phenylboronic acid (**2a**) as substrates. The reaction conditions and results were summarized in Table 1. Treatment with a mixture of **1a** and **2a**, $\text{Pd}_2(\text{dba})_3$ and L1 in THF at 80 °C in open air for 6 h, coupling product **3aa** was obtained in 31% yield (Table 1, entry 1). The yield decreased to 20% when using Cs_2CO_3 as base (Table 1, entry 2), whereas $^t\text{BuOK}$ was used as base, the yield of coupling product **3aa** was improved to 94% in THF under 70 °C (Table 1, entry 3). Dioxane and DMF were both effective for this reaction, but not better than THF under the same conditions (Table 1, entries 4 and 5). In the presence of L2, 77% product yield was obtained under the same conditions (Table 1, entry 7). Et_3N as base was not effective in this catalyst system (Table 1, entry 6). L2 is not better than L1, though the reaction temperature was improved to 110 °C in toluene (Table 1, entries 8 and 12). At room temperature, the yield of product **3aa** was reduced to 42% comparing with entry 3 (Table 1, entry 11). Only 60% yield was obtained when L3 was used as ligand (Table 1, entry 9). Notably, the reaction almost could not proceed without L1 ligand (Table 1, entry 13).

Under the optimized reaction conditions, the coupling reactions between a lot of aryl bromides and some arylboronic acids were carried out and the results were summarized in Scheme 2. As shown in Scheme 2, both electron-rich and electron-deficient aryl bromides were efficiently coupled with arylboronic acids to give biaryl

Table 1
Palladium-catalyzed Suzuki reaction of phenylbromide with phenylboronic acid^a.



Entry	Base	Solvent	T/°C	Ligand	Yield (%) ^b
1	K_2CO_3	THF	80	L1	31
2	Cs_2CO_3	THF	80	L1	20
3	$^t\text{BuOK}$	THF	70	L1	94
4	$^t\text{BuOK}$	Dioxane	70	L1	73
5	$^t\text{BuOK}$	DMF	70	L1	80
6	Et_3N	THF	80	L1	Trace
7	$^t\text{BuOK}$	THF	70	L2	77
8	$^t\text{BuOK}$	Toluene	110	L2	83
9	$^t\text{BuOK}$	THF	70	L3	60
10	$^t\text{BuOK}$	Toluene	70	L1	52
11	$^t\text{BuOK}$	THF	19(rt)	L1	42
12	$^t\text{BuOK}$	Toluene	110	L1	93
13	$^t\text{BuOK}$	THF	70	-	10

^a $\text{Pd}_2(\text{dba})_3$ (2.0 mol%), **1a** (2.0 mmol), **2a** (2.0 mmol) and ligand (4.0 mol%) in 10 mL of the indicated solvent at indicated temperature for 6 h.

^b Isolated yield.

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