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Platinum-catalyzed cross-couplings of organoboronic acids with aryl iodides

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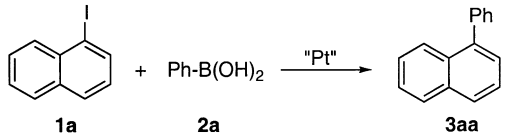
Abstract—Tetrakis(triphenylphosphine)platinum in DMF was utilized as a mild catalyst for cross-coupling reactions of organoboronic acids with aryl iodides. The present reactions exhibited excellent group-selectivity where couplings of organoboronic acids **2a**–**e** with 4-bromo-1-iodobenzene (**4**) give 4-arylbromobenzenes **5a**–**b** and 4-alkenylbromobenzenes **5c**–**e** in excellent yields. © 2002 Elsevier Science Ltd. All rights reserved.

Palladium-catalyzed cross-coupling of organoboronic acids with aryl bromides, iodides, or triflates, known as Suzuki reaction, is a versatile synthetic method for carbon–carbon bond formation.[1] Since a variety of organoboron derivatives are now available, stable in air, and inert to various functional groups, a number of studies on transition-metal-catalyzed cross-coupling reactions of organoboronic acids have been reported. But less reactive aryl chlorides do not undergo these cross-couplings except when they are activated by electron-withdrawing groups,[2] co-catalysts,[3] or additives.[4] Alternatively, cross-coupling of the aryl chlorides with arylboronic acids has been accomplished by use of nickel catalysts.[5]

We have initiated a research program to search a more selective metal catalyst capable of differentiating the iodide and the bromide of the substrates and found a preliminary solution from platinum-catalyzed reactions in DMF solvent. Various platinum compounds can

Table 1. Platinum-catalyzed cross-coupling reactions of phenylboronic acid **2a** with 1-iodonaphthalene **1a**



(1)

Entry	Pt-catalyst (2 mol%)	Base (2 equiv.)	Solvent	Temp. (°C)/time (h)	Yield (%)
1	$Pt(PPh_3)_4$	Cs_2CO_3	Ethanol	Reflux/12	26
2	$Pt(PPh_3)_4$	Cs_2CO_3	Water	Reflux/12	Trace
3	$Pt(PPh_3)_4$	Cs_2CO_3	1,4-Dioxane	Reflux/12	15
4	$Pt(PPh_3)_4$	Cs_2CO_3	CH_3CN	Reflux/12	19
5	$Pt(PPh_3)_4$	Cs_2CO_3	DMF	120/12	88
6	$Pt(PPh_3)_4$	K_2CO_3	DMF	120/12	46
7	$Pt(PPh_3)_4$	NaOH	DMF	120/12	15
8	$Pt(PPh_3)_4$	KF	DMF	120/12	19
9	$Pt(PPh_3)_4$	$Ba(OH)_2$	DMF	120/12	10
10	$PtCl_2$	Cs_2CO_3	DMF	120/12	Trace
11	$PtCl_4$	Cs_2CO_3	DMF	120/12	Trace
12	$PtCl_2/PPh_3$	Cs_2CO_3	DMF	120/12	Trace

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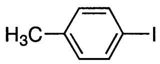
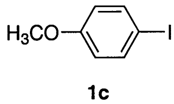
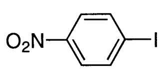
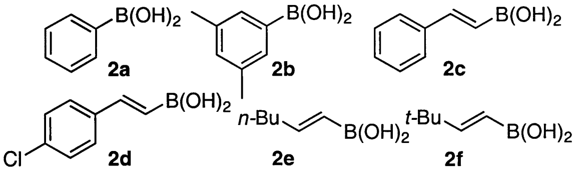
catalyze Boron–E (E = B, Si, Sn) additions to unsaturated bonds to give the organoboron compounds.[6] It is well-known that the hydrosilylation of terminal alkynes with dialkylchlorosilanes can be accomplished by a platinum catalyst (H_2PtCl_6, Speier's catalyst).[7] If such organoboron, organosilicon, or organotin compounds could undergo cross-coupling reactions with organic halides by a platinum catalyst, a very efficient tandem C–C bond-forming reaction can be developed. A few studies on platinum-catalyzed carbon–carbon bond-forming reactions have been reported. $Pt(PPh_3)_4$-catalyzed carbonylative cross-coupling of alkyl iodides with sodiumtetraphenylborate gave the corresponding phenylalkylketones in 40–60% yields.[8] Two bis(phosphine)platinum complexes were developed as catalysts for the cross-coupling of arylmagnesium halides with alkenyl bromides to give up to 95% of the products.[9] Recently, vinylation of aryl iodides using $Pt(COD)Cl_2$/PPh_3 as a catalyst system was also reported.[10] Platinum compounds compared to the corresponding Ni- or Pd compounds might have the low reactivity toward organic halides presumably due to diffused d-orbitals (5d-orbital). We expected that such low reactivity of platinum compounds could be utilized selective cross-coupling reactions of organoboronic acids with organic iodides in the presence of other labile functional groups such as organic bromides.

As a starting point of our study, we investigated the catalytic effect of three commercially available platinum compounds for cross-couplings of 1-iodonaphthalene (**1a**) with phenylboronic acid (**2a**) (Eq. (1)) and summarized the results in Table 1. When the reaction was screened with a catalytic amount of $Pt(PPh_3)_4$ in various solvents such as ethanol, water, 1,4-dioxane, acetonitrile, and DMF (entries 1–5), DMF was found to be an extraordinarily good solvent. Then, we tested various bases such as K_2CO_3, NaOH, KF, and Cs_2CO_3 in DMF (entries 6–9). The best result gave 1-phenylnaphthalene (**3aa**) in 88% isolated yield when the reaction was carried out with Cs_2CO_3 as a base at 120°C in DMF. The reaction did not complete at low temperature (100°C) even after 24 h. For the platinum's oxidation state, only the electron-rich Pt(0) compound could catalyze the cross-coupling reaction, suggesting that the rate-determining step of this reaction be the oxidative addition of platinum compound to the C–I bond of 1-iodonaphthalene. A general procedure is as follows. A mixture of 1-iodonaphthalene (86.0 mg, 0.33 mmol), Cs_2CO_3 (216.0 mg, 0.66 mmol), and phenylboronic acid (50.0 mg, 0.40 mmol) in dry *N*,*N*-dimethylformamide (2.0 mL) was treated with 2 mol% of $Pt(PPh_3)_4$ (8.5 mg, 6.6 μmol) and stirred at 120°C for 12 h under argon atmosphere. Extractive work-up and flash silica gel chromatography (EtOAc:hexane = 1:40) gave 1-phenylnaphthalene (**3aa**, 59.3 mg) in 88% yield.

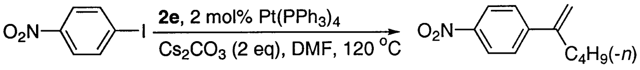
Table 2. Platinum-catalyzed cross-coupling reactions of arylboronic acids **2a–f** with aryliodides **1b–d**

$$\underset{\textbf{1b-d}}{\text{Ar–X}} + \underset{\textbf{2a-f}}{(HO)_2B\text{–}R} \xrightarrow[\text{DMF, 120 °C, 12h}]{\text{2 mol\% }Pt(PPh_3)_4,\ Cs_2CO_3\text{ (2 eq)}} \underset{\textbf{3ba-df}}{\text{Ar–R}} \qquad (2)$$

Ar-X	Boronic acids	Products (%yield)
 **1b**	**2a**	**3ba** (66)
	2b	**3bb** (95))
	2c	**3bc** (58)
	2d	**3bd** (70)
	2e	**3be** (72)
	2f	**3bf** (94)
 **1c**	**2a**	**3ca** (68)
	2b	**3cb** (84)
	2c	**3cc** (68)
	2d	**3cd** (67)
	2e	**3ce** (84)
	2f	**3cf** (76)
 **1d**	**2a**	**3da** (64)
	2b	**3db** (83)
	2c	**3dc** (79)
	2d	**3dd** (86)
	2e	**3de** (70)
	2f	**3df** (90)



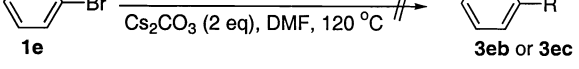
The dramatic solvent dependency is highly interesting although not yet clear. Based on the literature, we propose that the platinum compound might be activated by DMF and then oxidatively added to iodonaphthalene.[11] From the synthetic viewpoint of these results, we investigated a scope of these cross-coupling reactions of aryl iodides **1b–d** with various organoboronic acids **2a–f** under the similar conditions (Eq. (2) and Table 2).[12] The three representative aryl iodides were 4-iodotoluene, electron-poor 4-iodonitrobenzene, and electron-rich 4-iodoanisole. Cross-couplings of aryl iodides **1b–d** with arylboronic acids **2a–b** and with alkenylboronic acids **2c–f** occurred smoothly in 58–90% yields. It should be noted that the cross-coupling reaction of 4-iodonitrobenzene **1d** with hexenylboronic acid **2e** gave the unusual head-to-tail-cross-coupling product in 70% yield (Eq. (3)).[13]



1d **3de** (70 %)

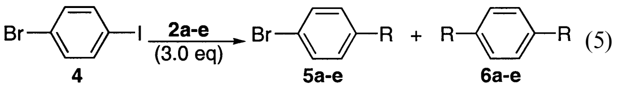
(3)

Overall, the yields of the coupling products were comparable to those of the Suzuki reactions, although the reaction temperatures were relatively high (120°C). In contrast to aryl iodides, bromobenzene (**1e**) did not undergo cross-coupling reactions with either **2b** or **2c** under these conditions (Eq. (4)). Such low reactivity of the platinum compounds to aryl halides suggested that the present reaction could be of a good synthetic potential as a chemoselective cross-coupling method.



1e **3eb** or **3ec** (4)

Table 3. Platinum-catalyzed cross-coupling reactions of organoboronic acids with 4-bromo-1-iodobenzene (**4**)



Entry	Boronic acids	Conditions[a]	Product ratio[b]	Combined yields (%)
1	**2a**	A	**5a** only	80
		B	**5a**:**6a** = 1:9	84
2	**2b**	A	**5b** only	92
		B	**5a**:**6a** = 1:4	78
3	**2c**	A	**5c** only	65
		B	**5a**:**6a** = 1:1	80
4	**2d**	A	**5d** only	80
		B	**5a**:**6a** = 1:2	92
5	**2e**	A	**5e** only	82
		B	**5a**:**6a** = 2:1	87

[a] Conditions A: Cs_2CO_3 (2 equiv.), 5 mol% $Pt(PPh_3)_4$, DMF, 120°C, 24 h. Conditions B: aq. 2 M Cs_2CO_3 (5 equiv.), 5 mol% $Pd(PPh_3)_4$, DMF, 50°C, 2 h.

[b] The ratios were determined by GC integrals.

Thus, cross-couplings of the organoboronic acids **2a**–**e** with 4-bromo-1-iodobenzene (**4**) were carried out under both palladium- and platinum catalysis (Eq. (5), Table 3).

The present method required 3.0 equiv. of organoboronic acids (**2a**–**e**) and 5 mol% of the platinum catalyst. Under these conditions, both aryl- (**2a**–**b**) and alkenylboronic acids (**2c**–**e**) were cleanly cross-coupled with the carbon–iodide bond of 4-bromo-1-iodobenzene (**4**) to give 4-aryl-1-bromobenzene (**5a**–**b**) and 4-alkenyl-1-bromobenzenes (**5c**–**e**) in excellent yields, respectively. On the other hand, palladium-catalyzed cross-coupling of organoboronic acids **2** (3 equiv.) gave a mixture of the double-coupling products **6a**–**e** along with the mono coupling products **5a**–**e**, respectively. Even use of only 1 equiv. of organoboronic acids also gave a mixture of **5** and the **6**.

In summary, we have accomplished platinum-catalyzed reactions of aryl- or alkenylboronic acids with various aryl iodides in DMF to give the cross-coupling products in good to excellent yields. Especially, the present method has shown excellent chemoselectivities in the cross-coupling of 4-bromo-1-iodobenzene (**4**) with organoboronic acids (**2a**–**e**) to give 4-aryl-1-bromobenzene (**5a**–**b**) and 4-alkenyl-1-bromobenzenes (**5c**–**e**) in excellent yields.

Acknowledgements

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