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## Phosphine-Free Palladium-Catalyzed Cross-Coupling of Tris(1-naphthyl)borane with Aryl Halides and Iodonium Salts

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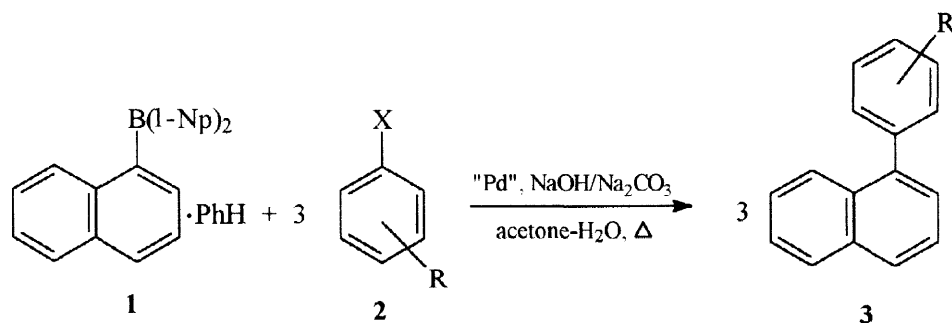
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**Abstract:** The catalytic cross-coupling reactions of the benzene complex of tris(1-naphthyl)borane with aryl halides and diaryliodonium salts are shown to occur smoothly in aqueous acetone or water in the presence of  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$  using  $\text{PdCl}_2$  as the catalyst precursor and give 1-arylnaphthalenes in high yields. © 1998 Elsevier Science Ltd. All rights reserved.

The development of synthetic methods for the preparation of polyfunctional biaryls remains an important problem in organic chemistry. Perhaps the most useful approaches are based on Pd-catalyzed cross-coupling reactions of organotin (the Stille coupling)<sup>1</sup>, arylboranes (the Suzuki coupling)<sup>2</sup> and Grignard reagents<sup>3</sup> with aryl halides or triflates containing functional groups. "Ligandless" palladium-catalyzed reactions of sodium tetraphenylborate with aryl halides<sup>4</sup> or diaryliodonium salts<sup>5</sup> under aqueous conditions are also attractive because all four phenyl groups of  $\text{Ph}_4\text{BNa}$  can be transferred in the presence of base. It would be interesting to extend this protocol to include sterically hindered arylboranes.

We report here that Pd-catalyzed reactions of the benzene complex<sup>6</sup> of tris(1-naphthyl)borane (**1**) with aryl halides (**2**) can be carried out in aqueous organic solvent or water in the presence of  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$  as a base (Table 1).



Suzuki<sup>2b</sup> has reported that the reaction of sterically hindered arylboronic acids proceeds slowly and gives poor yields of cross-coupled products due to steric hindrance.

The cross-coupling of complex **1** (1 equiv.) and aryl halides (3 equiv.), bearing various functionalities, proceeds smoothly at 65–84°C in the presence of 1 mol.% of phosphine-free palladium catalyst to give high

yields of 1-arylnaphthalenes. PdCl<sub>2</sub> was used as a catalyst precursor. It is noteworthy that under these conditions all three naphthyl groups of (1-Np)<sub>3</sub>B participate in the reaction.

Table 1. Cross-Coupling Reaction of (1-Np)<sub>3</sub>B-PhH with ArX and Ar<sub>2</sub>IX<sup>8, 9</sup>

Entry	ArX/Ar <sub>2</sub> IX	Solvent	Base (mol. eq.)	T, °C	t, h	Yield <sup>a</sup> of 1-NpAr, %
1	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> I	acetone-H <sub>2</sub> O (3.5:1.5)	NaOH (3)	20	150	37
2 <sup>b</sup>	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> I	acetone-H <sub>2</sub> O (3.5:1.5)	NaOH (3)	20	150	69
3	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> I	acetone-H <sub>2</sub> O (3.5:1.5)	Na <sub>2</sub> CO <sub>3</sub> (2)	65	0.5	74
4	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> I	acetone-H <sub>2</sub> O (3.5:1.5)	NaOH (3)	75	0.75	92 (82)
5	<i>m</i> -HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> I	acetone-H <sub>2</sub> O (3:2)	K <sub>2</sub> CO <sub>3</sub> (2)	75	1.5	83 (80)
6	<i>m</i> -HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> I	acetone-H <sub>2</sub> O (3:2)	NaOH (3)	84	1.5	- (92)
7	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> I	acetone-H <sub>2</sub> O (3:2)	NaOH (3)	75	1.0	56
8	<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> I	acetone-H <sub>2</sub> O (3:2)	Na <sub>2</sub> CO <sub>3</sub> (2)	75	0.75	- (73)
9	<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> I	acetone-H <sub>2</sub> O (3:2)	NaOH (3)	84	2.5	- (77)
10	<i>p</i> -NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br	DMF-H <sub>2</sub> O (3:2)	Na <sub>2</sub> CO <sub>3</sub> (2)	80	1.0	- (60)
11	<i>p</i> -NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br	H <sub>2</sub> O	NaOH (3)	84	4.0	- (38)
12	<i>p</i> -HOC <sub>6</sub> H <sub>4</sub> Br	H <sub>2</sub> O	NaOH (3)	75	3.0	52
13	<i>p</i> -HOC <sub>6</sub> H <sub>4</sub> Br	acetone-H <sub>2</sub> O (3.5:1.5)	NaOH (3)	80	7.5	26
14	<i>p</i> -HOC <sub>6</sub> H <sub>4</sub> Br	H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub> (2)	60	1.5	48
15	<i>p</i> -AcC <sub>6</sub> H <sub>4</sub> Br	acetone-H <sub>2</sub> O (3.5:1.5)	NaOH (3)	80	2.5	- (89)
16	<i>p</i> -NCC <sub>6</sub> H <sub>4</sub> Br	acetone-H <sub>2</sub> O (3.5:1.5)	NaOH (3)	84	5.0	98 (73)
17	<i>p</i> -NCC <sub>6</sub> H <sub>4</sub> Br	acetone-H <sub>2</sub> O (3:2)	K <sub>2</sub> CO <sub>3</sub> (2)	57	8.0	94
18	Ph <sub>2</sub> IBF <sub>4</sub>	acetone-H <sub>2</sub> O (4:1)	Na <sub>2</sub> CO <sub>3</sub> (2)	70	1.2	100
19	( <i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> ICF <sub>3</sub> CO <sub>2</sub>	acetone-H <sub>2</sub> O (3.5:1.5)	Na <sub>2</sub> CO <sub>3</sub> (2)	60	2.5	79

<sup>a</sup>) TLC-UV yields are based on ArX, and the isolated yields are in parentheses.

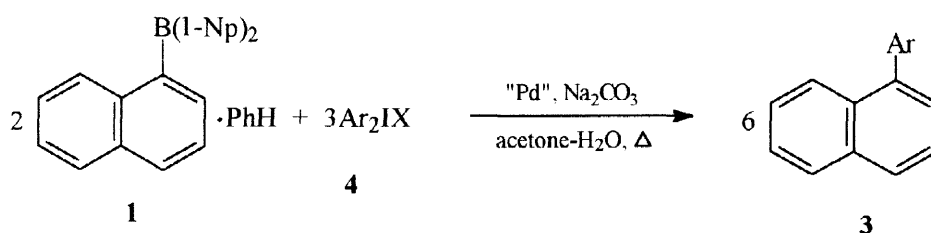
<sup>b</sup>) 1 mol.% Pd(dba)<sub>2</sub>; 21% of ArX remains unreacted.

These results are in good agreement with our recent investigations which show that phosphine-free palladium in aqueous medium in the presence of a base is a highly effective catalytic system for arylation of olefins<sup>7</sup> and cross-coupling of organoboranes with aryl halides<sup>10</sup> and acyl chlorides.<sup>11</sup>

The cross-coupling of tris(1-naphthyl)borane with iodoarenes can be carried out at room temperature, but the reaction proceeds very slowly (Table 1, entry 1,2); at elevated temperature it occurs more rapidly. There is no considerable difference in reactivity between aryl halides containing either electron-donating or electron-withdrawing groups (Table 1, entries 4 and 8, 4 and 10, 9 and 14). Water strongly effects the reaction, for

example, the cross-coupling of *p*-iodoanisole with (1-Np)<sub>3</sub>B occurs slowly in anhydrous organic solvents (acetone, Na<sub>2</sub>CO<sub>3</sub>, 71°C, 6h, 48%), but proceeds easily in a mixture of acetone (or DMF) and water despite the lower solubility of ArX (Table 1, entry 4). In some cases relatively weak bases such as Na<sub>2</sub>CO<sub>3</sub> give higher product yields (Table 1, entries 12 and 14).

We examined also the Pd-catalyzed reaction of complex **1** with diaryliodonium salts. Kang<sup>12</sup> has reported that aryl boronic acids were readily coupled with iodonium salts under aqueous conditions in the absence of base to give a mixture of cross-coupling products and aryl iodides. In the presence of base all aryl groups of sodium tetraphenylborate and diaryliodonium salt are consumed in the cross-coupling.<sup>5</sup> We found that the cross-coupling reaction of tris(1-naphthyl)borane with diaryliodonium salts **4** under basic-aqueous conditions in the presence of phosphine-free PdCl<sub>2</sub> affords the 1-arylnaphthalenes as the sole product (Table 1, entries 18, 19).



Complex **1** (2 equiv.) reacts with diaryliodonium salts **4** (3 equiv.) in aqueous acetone in the presence of Na<sub>2</sub>CO<sub>3</sub> at 60-70°C for 1.2-2.5 h to give the 1-arylnaphthalenes in high yields.

In conclusion, the palladium-catalyzed cross-coupling of sterically hindered tris(1-naphthyl)borane with aryl halides and diaryliodonium salts proceeds readily under mild and aqueous conditions to provide a convenient procedure for the synthesis of 1-arylnaphthalenes from available starting reagents.

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8. In a typical experiment (1-Np)<sub>3</sub>B•PhH (0.1645 g, 0.35 mmol), *m*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>I (0.249 g, 1 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.212 g, 2 mmol) and aqueous 0.1M PdCl<sub>2</sub> (0.1 mL, .01 mmol) was vigorously stirred at 75°C for 0.75 h. After cooling the reaction mixture was treated by diluted HCl and extracted with ether. The residue was recrystallized from heptane to give pure sample.
9. All products were characterized by UV, <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy and element analysis.
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