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# Polymer-bound Palladium-catalyzed Cross-coupling of Organoboron Compounds with Organic Halides and Organic Triflates

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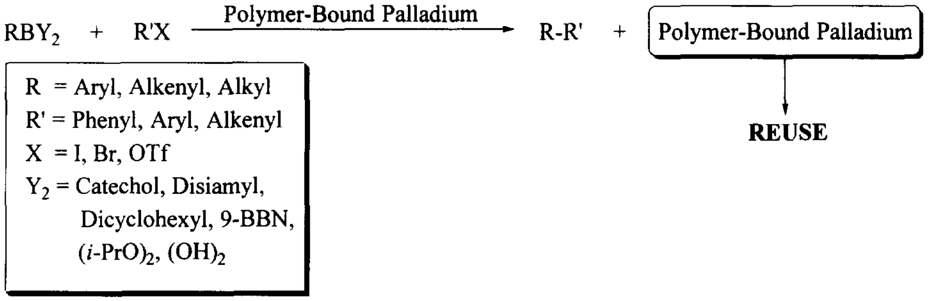
**Abstract:** The polymer-bound palladium-catalyzed cross-coupling reaction of electrophiles(i.e., halides and triflates) with organoboron compounds to form carbon-carbon bonds was achieved at mild conditions with very high activity in the Suzuki coupling reaction. The polymeric catalyst can be easily separated from a reaction mixture and reused more than 10 times with no decrease in activity

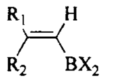
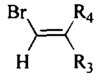
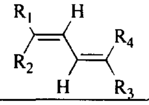
The palladium-catalyzed cross-coupling of organoboranes such as boronic acids, boronates, and trialkylboranes with organic electrophiles(i.e., halides and triflates) in the presence of base is known as the Suzuki reaction[1] and has become an extremely powerful tool in organic synthesis. These coupling reactions tolerate many functional groups, yield easily removable nontoxic and readily available organoboranes. Concequently, they are utilized extensively in the synthesis of natural products.

The development of useful reactions catalyzed by soluble transition metal has led to interest in evolving "solublized" versions of these catalysts for ease of recovery and work-up.[2] Hybrid catalysts combining the attributes of conventional homogeneous catalysts with the experimental simplicity of heterogeneous catalysts have been proven to be fruitful subjects for research by both academic and industrial chemists. [3] Polystyrene -supported palladium catalysts have been successfully used for a variety of organic reactions.[4] Quite a few reports have appeared in which such catalysts are bound to various sorts of polymer.[5-8] Hallberg and co-workers have studied various carbon-carbon bond forming reactions, such as the Heck arylation, [8] using similarly prepared catalysts. However, there is no specific papers regarding polymer-bound palladium-catalyst for the Suzuki coupling reaction. In order to expand the use of the catalysis of the palladium(0) complex to many other organic reactions, we first have tried useful Suzuki coupling reactions of organoboron compounds and electrophiles using our polymer-bound palladium(0) complex. [7,8,9] We describe herein the characteristic features of the polymer-bound palladium catalyst for various kinds of Suzuki coupling reactions which are shown in Scheme 1.



**Scheme 1**

**Table 1.** Polymer-bound Palladium-catalyzed Cross-coupling Reaction of Organoboranes with 1-Alkenyl Bromides or Iodobenzene[a]

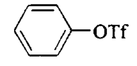
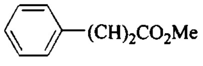
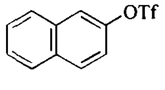
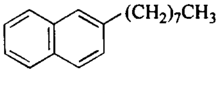
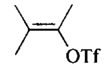
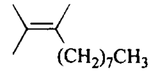
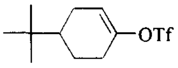
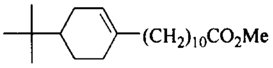
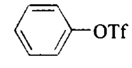
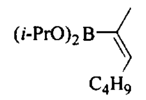
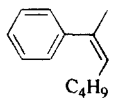
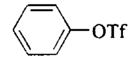
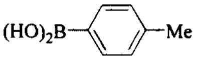
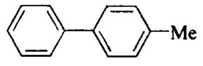
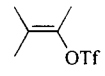
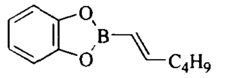
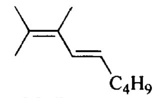
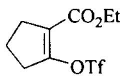
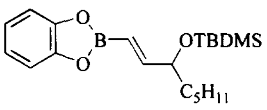
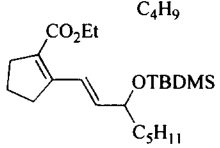
| Entry |  | | |  | |  |
|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $X_2$ | $R_3$ | $R_4$ | Yield[b](%) |
| 1 | Ph | H | BDOB | H | Ph | 96(89) |
| 2 | Bu | H | BDOB | Ph | H | 91(80) |
| 3 | Bu | H | BDOB | H | Ph | 94(86) |
| 4 | Bu | H | Sia | Ph | H | 82(59) |
| 5 | Bu | H | BDOB | Hex | H | 89(86) |
| 6 | Bu | H | BDOB | H | Hex | 84(88) |
| 7 | H | Bu | BDOB | H | Ph | 89(42) |
| 8 | H | Bu | Sia | Ph | H | 88(55) |
| 9 | H | Bu | Sia | H | Hex | 85(49) |
| 10 | Ph | H | BDOB | Me | Me | 81(28) |
| 11 | Ph | H | Sia | Me | Me | 78(52) |
| 12 | H | Bu | Sia | PhI | | 81(58) |
| 13 | H | Bu | Cyclohexyl | PhI | | 79(49) |

[a]The reaction was carried out at 80 °C for 2 h under nitrogen, by using polymer-bound palladium(1 mol % palladium), NaOEt(2 equiv), organic halide(1 equiv) ,and organoboron(1.2 equiv). [b]The yields were isolated yields and the yields in parentheses are those obtained in the same conditions,except palladium catalyst, here we used $Pd(PPh_3)_4$ as the palladium catalyst

The results of polymer-bound palladium-catalyzed cross-coupling reaction of organoboranes with 1-alkenyl bromide[10] or iodobenzene are summarized in Table 1. The (*E*)-β-styryl-1,3,2-benzodioxaborole was reacted with (*Z*)-β-styrylbromide in the presence of polymer-bound palladium(1 mol % palladium), sodium ethoxide(2 equiv) at 80 °C in benzene for 2 h to afford (*1Z, 3E*)-diphenylbutadiene in 96 % yield(entry 1) with retaining the original configurations of the organoborane and the alkenyl bromide. Treatment of (*Z*)-1-butenyl-

1,3,2-benzodioxaborole with (*Z*)-β-styryl bromide in the same conditions afforded (*1Z, 3Z*)-1-phenyl-1,3-octadiene in 89 % yield(entry 7). Finally, for (*Z*)-1-butenyl-dicyclohexyl borane with iodobenzene in the same conditions afforded (*Z*)-1-phenyl-2-butene in 79 % yield(entry 13).

**Table 2.** Polymer-bound Palladium-catalyzed Cross-coupling Reaction of Organoboranes with Triflates[a]

| Entry | Triflate | Organoborane | Reaction Time(hrs) | Product | Yield[b](%) |
|---|---|---|---|---|---|
| 1 |  | 9-BBN-$(CH_2)_{10}CO_2Me$ | 5 |  | 88(87) |
| 2 |  | 9-BBN-$(CH_2)_7CH_3$ | 5 |  | 87(82) |
| 3 |  | 9-BBN-$(CH_2)_7CH_3$ | 6 |  | 90(91) |
| 4 |  | 9-BBN-$(CH_2)_{10}CO_2Me$ | 5 |  | 91(99) |
| 5 |  |  | 5 |  | 85(68) |
| 6 |  |  | 5 |  | 90(83) |
| 7 |  |  | 6 |  | 98(99) |
| 8 |  |  | 11 |  | 97(96) |

[a] The reaction was carried out in dioxane at 85 °C for 5 - 11 h by using polymer-bound palladium(1 mol % palladium), $K_3PO_4$(1.5 equiv), triflate(1 equiv) and organoboron(1.1 equiv). [b] The yields were isolated yields and the yields in parentheses are those obtained in the same conditions, except palladium catalyst, here we used $Pd(PPh_3)_4$ as the palladium catalyst.

Alternatively, we have investigated polymer-bound palladium-catalyzed cross-coupling reaction of triflates with 9-alkyl-9-BBN derivatives or 1-alkenyl- and aryl boron compounds[11] in order to achieve the coupling between triflates[11] and organoboron compounds which is summarized in Table 2. The 9-(10-carbomethoxydecanyl)-9-BBN was reacted with phenyl triflate in the presence of polymer-bound palladium(1 mol % palladium), $K_3PO_4$(3 equiv) at 85 °C in dioxane for 5 h to afford (10-carbomethoxydecanyl)benzene in 88 % yield(entry 1). Treatment of 9-(10-carbomethoxydecanyl)-9-BBN with 4-*tert*-butylcyclohexenyl triflate in the same conditions afforded methyl-11-(4-*tert*-butylcyclohexenyl)undecanoate in 91 % yielde(entry 4). Treatment of *p*-toluylboronic acid with phenyl triflate in the same conditions afforded *p*-methylbiphenyl in 90 % yield(entry 6). Finally, for 2-[(*E*)-1-hexenyl]-1,3,2-benzodioxaborole with 3-methyl-2-buten-2-yl triflate in the same conditions afforded (*4E*)-2,3,-dimethyl-2,4-nonadiene in 98 % yield(entry 7).

Typically, as in the reactions described above(Table 1 and Table 2), recycling the palladium catalyst was quite successful here. We recycled the polymer-bound palladium catalyst at least 5 times. However, in most cases, the catalyst was used more than 10 times with no decrease in activity. The catalyst was recycled more than 10 times with maintaining the yield which was given in first catalytic cycle(Total turnover number of > 500 mmol product / mmol of catalyst).

In summary, the polymer-bound palladium-catalyzed cross-coupling reaction of electrophiles(i.e., halides and triflates) with organoboron compounds to form carbon-carbon bonds was achieved at mild conditions. Catalytic activity is comparable to that of a close homogeneous analogue $Pd(PPh_3)_4$.[11-12]

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11. Suzuki, A.; Miyaura, N.; Ohe, T. *J. Org. Chem.* **1993**, *58*, 2201.
12. Preparation of polymer-bound Pd(0) Complex: The polystyrene resin with a 100% chloromethylated aromatic ring was treated with $LiPPh_2$ at 25 $^{o}$C for 48 h. The reaction of the phosphinated resin(5 g) with $PdCl_2$(0.75 g) in a molar ratio of P/Pd of 3 was carried out to give a yellow polymeric d(II) complex. The Pd(II) complex(5 g, 3.71 mmol of Pd) was added to ethanol(50 mL) containing $PPh_3$(2.09 g, 7.42 mmol). The mixture was stirred at rt for 3 h. Then hydrazine hydrate(1.87 g, 3.71 mmol) was added to the mixture, and stitting was continued for 2 h. The resulting polymer was filtered, washed with ethanol and ether, and dried under vacuum to give a dark green polymer complex. All above procedures were carried out under a nitrogen atmosphere. The analysis showed the following: C, 74.51%; H, 5.67%; Cl, 2.76%,; P, 9,15%. This corresponds to a ratio of P/Pd of 3.9, where the palladium content was calculated by difference.

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