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Palladium Chloride/Tetraphenylphosphonium Bromide Intercalated Clay: New Catalyst for Cross-coupling of Aryl Halides with Arylboronic Acids

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Abstract: A facile method for the preparation of biaryl compounds is described from readily accessible aryl halides and arylboronic acids using palladium chloride/tetraphenylphosphonium bromide intercalated clay as a new catalyst. © 1998 Elsevier Science Ltd. All rights reserved.

The Suzuki coupling reactions of aryl halides with arylboronic acids or esters provides ready access to biaryl compounds and has become a valuable tool for the organic chemists.[1-4] The low toxicity, stability and ease of handling of boronic acids have made them among the most popular intermediates for cross-coupling reactions with a variety of substrates. Several reports on cross-coupling reactions of arylboronic acid and aryl halides using palladium[5] or nickel[6,7] complexes and extension of these reactions to sulfonium salts[8] are described. The milder coupling conditions and flexibility are some of the main advantages that render boronic acids as the ideal reagents in combinatorial chemistry.[9,10] Recently, the reaction of arylboronic acid catalyzed by pre-formed palladium and palladium-nickel clusters[11] has been reported in phosphine-free coupling with arene diazonium fluoroborates[12,13] and synthesis of neoflavones by arylation of coumarin-4-triflates.[14] In these examples, the regenerated catalyst is difficult to isolate and further processing is necessary for any subsequent reaction. Consequently, for the sake of catalyst efficiency and reusability in industrial context, the development of new catalysts is desired. Clays and their various cation-exchanged forms, clay-supported reagents and pillared clays find extensive applications in organic synthesis under mild reaction conditions.[15-20] These modified clay materials, unlike other conventional catalysts, enjoy considerable advantages such as ease of handling, recyclability, low cost, easier modulation of acidity levels by suitable exchange of cations. Our interest in modified clay materials and their application in organic functional group transformations[20] prompted us to explore the synthesis of biaryl compounds using new catalyst system, palladium chloride and tetraphenylphosphonium bromide intercalated clay (Cat-I).

In a typical example, an equimolar amount (1 mmol) of aryl halide and arylboronic acid is refluxed with premixed catalyst and potassium carbonate in dimethylformamide (**Eqn.**) with continuous stirring for a specified time as shown in the table.

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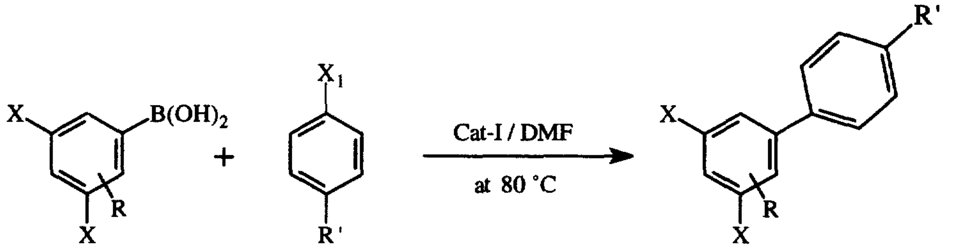


(Eqn.)

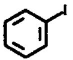
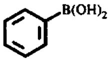
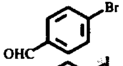
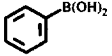
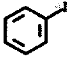
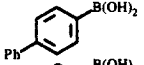
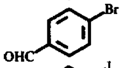
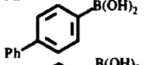
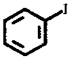
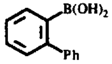
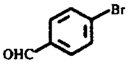
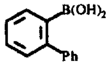
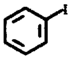
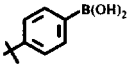
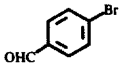
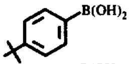
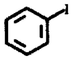
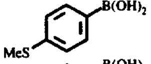
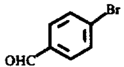
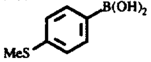
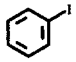
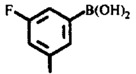
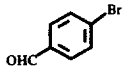
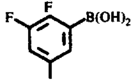
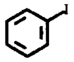
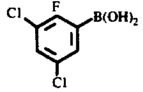
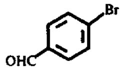
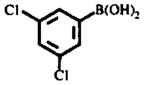
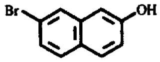
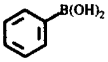
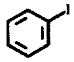
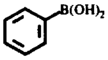
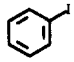
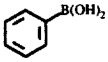
R = H, 2-Ph, 4-Ph, 4-SMe and 4-*tert*-butyl; R' = H, CHO
X = H, F and Cl; X_1 = I, Br

Our results for a variety of biaryl compounds are summarized in the Table. Arylboronic acids bearing an electron withdrawing substituents undergo the reaction at a faster rate as compared to arylboronic acid with electron releasing substituents appended. In the case of ortho substituted arylboronic acid, the rate of the reaction is slow when compared to para substituted acids due to large steric hindrance. The reaction rate using this heterogeneous catalyst is much faster, even at these very low concentration of the catalyst, when compared to homogeneous reaction conditions. We have also explored this reaction in aqueous media using ultrasound and observed the formation of biaryl compounds in good yields (entry 16).

In conclusion, these high yield reactions for the rapid assembly of biaryls are superior to the corresponding reactions in the homogeneous medium because of the organized assembly of aluminosilicate layers. The salient features of the protocol are the ease of handling of the reaction and the separation of the catalyst by simple filtration. The subsequent reuse (entry 17) of the catalyst (recycled twice) without any loss in activity makes this an ideal protocol and a useful and attractive alternative to the currently available methods.

General procedure for the synthesis of biaryl compounds:- In a typical experiment, the clay-based catalyst (20 mg, 0.01 mmol) and K_2CO_3 (276 mg, 2 mmol) were intimately mixed using a pestle and mortar and placed in a round bottomed flask. To this, equimolar amounts (1 mmol) of starting materials (arylboronic acid and aryl halide) were added followed by dimethylformamide (2 mL) and the mixture refluxed with continuous stirring for the specified time in the Table. After completion of the reaction, as monitored by TLC examination, the mixture was quenched with water and the product was extracted into ethyl acetate. The organic layer was washed with excess of water in order to remove any residual dimethylformamide. The product composition was determined by GC-MS analysis (Hewlett-Packard model 5890 gas chromatograph with a mass spectrometer) and the identity of the products were confirmed by spectral data. The clay material was retrieved from the aqueous layer by filtration, washed with organic solvent and dried overnight at 110 °C for further reuse (recycled twice) without any loss in catalytic activity (entry 17).

Table: Product distribution in Suzuki reaction catalyzed by palladium chloride/tetraphenylphosphonium bromide intercalated clay[a]

Entry	Starting Materials		Reaction Conditions (h)	% of different product		
				I	II	III
1			1	90	10	00
2			2	80	10	10
3			0.5	90	04	06
4			1	95	05	00
5			1	71	19	10
6			1.5	56	14	30
7			5	57	14	29
8			12	70	10	20
9			1	70	30	00
10			1.5	51	19	30
11			0.5	65	22	13
12			0.5	83	07	10
13			0.5	68	14	18
14			1	94	02	04
15			2	54	04	42
16[b]			1	89	00	11
17[c]			1	89	11	00

[a] The relative amounts of product formation are determined by GC-MS analysis; I is cross-coupling product; II is self coupling product from boronic acid and III is the starting aryl halides; the products exhibited physical and spectral properties in accord with the assigned structures; [b] using ultrasound irradiation in aqueous media; [c] using recycled catalyst (twice).

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