# Main-Chain NHC-Palladium Polymers as a Recyclable Self-Supported Catalyst in the Suzuki-Miyaura Coupling of Aryl Chlorides in Water

Babak Karimi\*, Pari Fadavi Akhavan

Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P.O. Box 45195-1159, Gava Zang, Zanjan, Iran.

# **Experimental Section**

**Materials and Methods**: Starting materials and solvents were purchased from common commercial sources and were used additional purification. The gas chromatography analysis was performed on a GC instrument. <sup>1</sup> H-NMR spectra were recorded at 250 MHz.

PhCH<sub>3</sub> was distilled from sodium and benzophenone under argon atmosphere prior to use. DMF was distilled under argon. DMSO for polymerization reactions was of reagent quality and used as obtained from commercial sources.

Formic acid was refluxed on Phetalic anhydride for 6h and distilled.

#### **Procedure for formation of Benzo-bis(imidazole)**:

1,2,4,5-Benzenetetraamine tetrahydrochloride (284 mg, 1.00 mmol) was poured into a round bottom flask was charged with a magnetic stir bar. Formic acid (88-99%) was added and the flask was fitted with an air-jacketed condenser. The reaction mixture was placed in an oil bath at 100 °C for 36 h. The reaction mixture was then allowed to cool, poured into ice-cold water (equal volume to formic acid) and neutralized with saturated K<sub>2</sub>CO<sub>3</sub> solution. Neutralization caused precipitation of the product which was collected via vacuum filtration, rinsed with cold water, and dried under vacuum over P<sub>2</sub>O<sub>5</sub> to produce the desired product as a light brown solid: mp > 300 °C; <sup>1</sup>H NMR (250 MHz, DMSO-*d*6, D<sub>2</sub>O)  $\delta$  7.651 (s, 2H), 8.156 (s, 2H); <sup>13</sup>C NMR (62.90 MHz, DMSO-*d*6)  $\delta$  99.67, 135.38, 143.01.



**Procedure for formation of Tetrabenzyl benzo-bis(imidazolium) bromide:** In a welldried two necked 100ml Schlenk flask, bis(imidazole) (576 mg, 3.64 mmol) was added to a solution of NaH (298 mg, 60 wt %, 7.46 mmol) in PhCH<sub>3</sub> (30 mL) under argon atmosphere. The resulting solution was heated to 110 °C for 1 h, after cooling the solution to room temperature, benzylbromide (2.61 mL, 21.84 mmol) was added via syringe. The suspension was placed in an oil bath at 110 °C for 1 h, then dry DMF (30 mL) was added via syringe and the reaction was maintained at 110 °C for 6 h, then 60 °C for 4 h. Upon completion, the suspension was allowed to cool, diluted with PhCH<sub>3</sub> (50 mL) and the solids were collected by vacuum filtration, rinsed with water and THF successively, and dried under vacuum over P<sub>2</sub>O<sub>5</sub> to give a tan powder: mp 280-282 °C (dec); <sup>1</sup>H NMR (250 MHz, DMSO-*d*6)  $\delta$  10.54 (s, 2H), 8.93 (s, 2H), 7.60-7.58 (m, 8H), 7.39-7.34 (m, 12H), 5.87 (s, 8H), <sup>13</sup>C NMR (62.90 MHz, DMSO-*d*6)  $\delta$  146.1, 133.4, 129.9, 128.9, 128.8, 128.6, 99.8, 50.5.



**Typical procedure for polymerization**: Bis(imidazolium) bromide (1.0 equiv.) was dissolved in DMSO (ca. 0.1-0.2 M) and either  $Pd(OAc)_2$  (1.0 equiv.), was added in one portion. The solution was placed in a preheated oil bath at 110 °C and stirred open-air for 1-5 h. The reaction mixtures typically darkened in color (to orange-brown) as the reaction progressed. The cooled reaction mixture was precipitated into H<sub>2</sub>O and the solids were collected via vacuum filtration and dried under vacuum.

Light brown solid. <sup>1</sup>H NMR (250 MHz, DMSO-*d*6) δ 5.30-6.50 (m, 8H), 6.80-7.70 (m, 22H).

General Procedure for the Suzuki coupling of Aryl chlorides using catalyst 1 (Pd loading = 0.0005 mol%, for iodo- and bromoarenes): A mixture of aryl halide (1 mmol), aryl boronic acid (1.2 mmol), potassium carbonate (415 mg, 3 mmol), and distilled water (3 mL) was stirred vigorously under the condition indicated in Table 1. A solution of catalyst 1 in DMSO (0.15 ml, 5.8 ppb Pd, 0.0005 mol%) was then rapidly injected to the reaction mixture. The progress of the reaction was monitored by GC. After completion of the reactions, the mixture was cooled to room temperature and the catalyst was separated by filtration and washed with diethyl ether. The aqueous phase was then extracted four times with diethyl ether (4×10 ml). The organic phase was combined together and dried over MgSO<sub>4</sub>, and diethyl ether was evaporated under reduced pressure. The final biaryl product was isolated by column chromatography and characterized by nuclear magnetic resonance spectroscopy (NMR) and by gas chromatography (GC) using authentic samples.

General Procedure for the Suzuki coupling of Aryl chlorides using catalyst 1 (Pd loading = 0.05 ml%, for Chloroarenes): A mixture of aryl halide (5 mmol), aryl boronic acid (1.2 mmol), potassium carbonate (2.07 g, 15 mmol), catalyst 1 (10 mg, equiv. to 0.05 mol% by AA) and distilled water (15 mL) was stirred vigorously under the condition indicated in Table 1. The progress of the reaction was monitored by GC. After completion of the reactions, the mixture was cooled to room temperature and the catalyst was separated by filtration and washed with diethyl ether. The aqueous phase was then extracted four times with diethyl ether (4×50 ml). The organic phase was combined together and dried over MgSO<sub>4</sub>, and diethyl ether was evaporated under reduced pressure. The final biaryl product was isolated by column chromatography and characterized by nuclear magnetic resonance spectroscopy (NMR) and by gas chromatography (GC) using authentic samples.

**Procedure for Reusability Test of NHC-Pd Complex 1.** A mixture of 4chlorobenzaldehyde (1.41 g, 10 mmol), phenylboronic acid (1.34 g, 11 mmol), and  $K_2CO_3$ (4.15g, 30 mmol) and catalyst **1** (20 mg, equiv. to 0.05 mol % Pd by AA) and of in distilled water (30 mL) were placed in an oil bath at 80 °C under Ar atmosphere. After the completion of the reaction (Table 1), the resulting reaction mixture was filtered and the catalyst washed with distilled water and diethyl ether dried under vacuum at 40 °C. After the recovered polymer as a yellow powder was reused 6 times under the same reaction conditions as for the first run. The data resulting yields (GC yields) and the percent of the recovered catalyst are shown in Table 1S.

Run	GC Conversion (%)	Recovered catalyst (mg/%)
1	100	18.6/93
2	98	17.5/94
3	93	16.8/96
4	91	15.4/92
5	90	13.7/89
6	79	Total recovery = 69% recovery after 5 run

Table 1S. The recovery report for catalyst 1

### Procedure for study of Hg(0) effect on Complex 1 reactivity

A mixture of 3-boromo acetophenone (1 mmol), phenylboronic acid (1.2 mmol), Hg (0) (400 mg), potassium carbonate (415 mg, 3 mmol), and distilled water (3 mL) was stirred vigorously at 90 °C. A solution of catalyst **1** in DMSO (0.15 ml, 5.8 ppb Pd, 0.0005 mol%) was then rapidly injected to the reaction mixture. The progress of the reaction was monitored by GC. The corresponding biphenyl was obtained in 87% yields after 8h (GC yield). The same reaction in the absence of Hg(0) gave 89% GC conversion after 8 h under the same reaction condition without any detectable induction period.





































4-Ethyl-biphenyl













4'-methyl-biphenyl- 3-carbaldehyde













**Biphenyl-4-carbonitrile** 











4-Methoxy-biphenyl













0 H<sub>3</sub>C н

4'-methyl-biphenyl-4- carbaldehyde











1-Biphenyl-3-yl-ethanone













## 4'-Methyl-biphenyl-4-carbonitrile













Phenyl- 4-carbaldehyde













Phenyl- 4-carbaldehyde











4, 4'-Dimethyl-biphenyl













4'-Methyl-biphenyl-2-carbaldehyde

















**Biphenyl- 2-carbaldehyde** 











Biphenyl













4-Methyl-biphenyl









nda





----- 21.23



