

# Polymer-supported *N*-heterocyclic carbene–rhodium complex catalyst for the addition of arylboronic acids to aldehydes

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## Abstract

A novel polymer-supported *N*-heterocyclic carbene (NHC)–rhodium complex was prepared from chloromethyl polystyrene (CM PS) resin using a simple procedure. This polymer-supported NHC–rhodium complex was used as a catalyst for the addition of arylboronic acids to aldehydes affording arylmethanols in excellent yields.

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**Keywords:** *N*-Heterocyclic carbene–rhodium complex; Polymeric support; Heterogeneous catalyst; Rhodium; Arylation

## 1. Introduction

Diarylmethanols are important intermediates for the synthesis of biologically and pharmaceutically active substances [1–3]. The addition of organometallic reagents to aldehydes has been one of the general methods for the synthesis of diarylmethanols. Of these reagents, organolithium and organomagnesium compounds are most frequently used for this purpose, but tolerate only a few electrophilic groups on themselves [4–11]. Examples of using other functionalized organometallic species [12–19] such as organocopper, organochromium, organotin, especially organozinc, have been described. However, these organometallic reagents are usually toxic and sensitive to air and moisture. The progress that has been achieved by recent publications describing the addition of arylboronic acid derivatives to aldehydes in the presence of catalytic amounts of Rh (I) and phosphine, nitrogen [20–23], especially NHC ligands [24–29] deserve particular mention. These methods present high efficiency with a reasonable

tolerance towards polar substituents in the substrates and benefit from the stability and ready accessibility of the non-toxic boron derivatives.

Due to their versatile processing capabilities, ease of product/catalyst separation, immobilized catalysts offer many advantages for industrial applications. Although NHCs as ligands for transition metal complexes have found many successes in homogeneous catalysis [30,31], including addition of arylboronic acid derivatives to aldehydes, heterogenizing NHC–metal complexes still remain practically useful. The high dissociation energies of metal–carbon bonds in NHC–metal complexes make NHCs better ligands for heterogeneous systems than others, e.g., phosphine ligands. With these concerns, a few kinds of immobilized NHC–metal complexes have been developed. Polymer-supported 1,3-disubstituted-imidazoline-2-ylidene–Pd complexes have been applied in Suzuki cross-coupling [32–35] and Heck reactions [36]. Supported ruthenium complexes of both 1,3-disubstituted-imidazoline-2-ylidene and 1,3-disubstituted-imidazolidine-2-ylidene have been used in ring-closing metathesis [30]. Immobilized rhodium complexes of NHCs are scarce. Özdemir et al. reported a silica-supported rhodium complex of 1,3-disubstituted-imidazolidine-2-ylidene for the addition of phenylboronic acid

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to aldehydes [37]. Weberskirch described the immobilization of a 1,3-disubstituted-imidazoline-2-ylidene–Rh complex to a water-soluble, amphiphilic block copolymer for hydroformylation of alkene [38]. We report here the preparation of a novel polymer-supported 1,3-disubstituted-imidazoline-2-ylidene–Rh complex from chloromethyl polystyrene, and its application in the Rh-catalyzed addition of arylboronic acids to aldehydes.

## 2. Results and discussion

The imidazolium-loaded polymeric support (**1**) for Rh catalyst was prepared by treating *N*-(2,4,6-trimethylphenyl)imidazole with CM PS resin using a simple method (Fig. 1). Thus, a mixture of CM PS resin and an excess amount of (2,4,6-trimethylphenyl)imidazole was agitated in NMP at 80 °C for 48 h. The loading of imidazolium was determined to be 0.61 mmol/g by means of the nitrogen content obtained from elementary analysis. Since the activity of the polymer-supported catalyst is influenced by the swelling properties of the support in solvent, the swelling volume of imidazolium-loaded polymeric support (**1**) was measured (Table 1). Obviously, **1** has the largest swelling volume in dioxane.

The complex **2** formed after the mixture of  $[\text{Rh}(\text{COD})\text{Cl}]_2$  and the resulting resin (**1**) was shaken in THF for 24 h at room temperature in the presence of  $\text{KO}^t\text{Bu}$ , which played a role as a base for the deprotonation of the imidazolium group. FT-IR spectrum of **2** is obviously different from that of CM PS resin. An absorption at  $3398\text{ cm}^{-1}$  indicates the presence of physisorbed  $\text{H}_2\text{O}$ . In addition, there are NCN stretching bands at  $1545\text{ cm}^{-1}$  and an imide ring stretching vibration at  $1379\text{ cm}^{-1}$ . Thermogravimetry analysis (TGA) showed the weight loss on heating from 40 to 150 °C is less than

2% and might be attributed to the release of physisorbed water. Thermal degradation of **2** occurred at about 260 °C. The loading level of the immobilized rhodium was measured to be 0.18 mmol/g by inductively coupled plasma-atomic emission spectrometry (ICP-AES). This means that 29.0% of the imidazolium groups in the polymeric support (**1**) participated in the formation of Rh complex. The low loading of Rh implies that the majority of the complex formed between the Rh and imidazolium groups may be located within the surface layer of the polymeric support.

The catalytic activity of the polymer-supported NHC–Rh complex (**2**) was investigated for the addition of phenylboronic acid to *p*-chlorobenzaldehyde (Table 2). To optimize reaction conditions, we surveyed several reaction variables, such as reaction temperature, time and solvent. As shown in Table 2, excellent yield (95%, entry 12, Table 2) was successfully obtained with lower catalyst loading (0.35 mol%). Higher temperature (90 °C, entry 5, Table 2) and longer reaction time were generally favorable to the reaction (48 h, entry 7, Table 2). The reaction in a co-solvent consisting of 1,4-dioxane and water showed better results (entries 2 versus 8 and 9, Table 2). Furthermore, with decrease of the amount of water, the yield of the reaction increased greatly from 39.2% to 95% (entries 2, 10–12, Table 2), presumably due to the best swelling properties of the imidazolium-loaded polymeric support (**1**) in 1,4-dioxane (Table 1). However, poor result obtained when the reaction was preformed in 1,4-dioxane alone (entry 13, Table 2).

An assessment of the recycling potential of the polymer-supported NHC–Rh catalyst was made, using phenylboronic acid and *p*-chlorobenzaldehyde as substrates. We found that important factor affecting the stability and activity of the polymer-supported NHC–Rh catalyst **2**

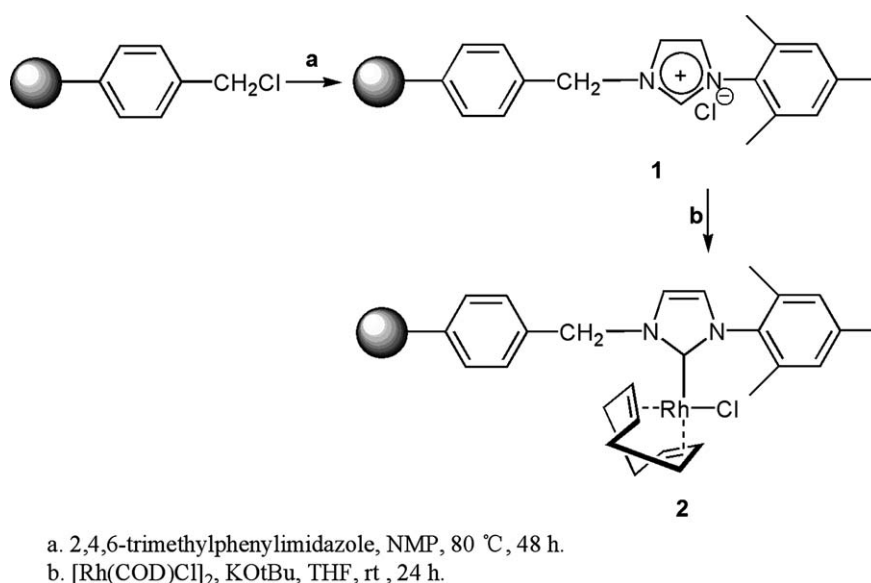


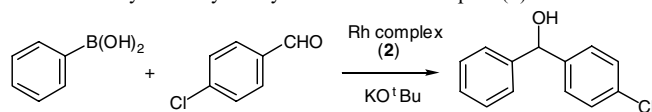
Fig. 1. Synthesis of imidazolium-loaded polymeric support (**1**) and polymer-supported NHC–Rh complex (**2**).

Table 1

Swelling volume in solvent (mL/g polymeric support) of the imidazolium-loaded polymeric support (**1**)

Dry	Water	DME	1,4-Dioxane	THF	MeOH
1.8	2.2	3.8	4.5	4.0	2.4

Table 2

Addition of phenylboronic acid to 4-chlorobenzaldehyde catalyzed by the NHC–Rh complex (**2**)<sup>a</sup>

Entry	Solvent (v:v)	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>
1 <sup>c</sup>	1,4-Dioxane/H <sub>2</sub> O (4:1)	80	24	70
2	1,4-Dioxane/H <sub>2</sub> O (4:1)	80	24	88
3 <sup>d</sup>	1,4-Dioxane/H <sub>2</sub> O (4:1)	80	24	89
4	1,4-Dioxane/H <sub>2</sub> O (4:1)	70	24	77
5	1,4-Dioxane/H <sub>2</sub> O (4:1)	90	24	89
6	1,4-Dioxane/H <sub>2</sub> O (4:1)	80	12	62
7	1,4-Dioxane/H <sub>2</sub> O (4:1)	80	48	89
8	DME/H <sub>2</sub> O (4:1)	80	24	71
9	THF/H <sub>2</sub> O (4:1)	80	24	33
10	1,4-Dioxane/H <sub>2</sub> O (2:1)	80	24	40
11	1,4-Dioxane/H <sub>2</sub> O (10:1)	80	24	92
12	1,4-Dioxane/H <sub>2</sub> O (100:1)	80	24	95
13	1,4-Dioxane	80	24	63
14 <sup>e</sup>	1,4-Dioxane/H <sub>2</sub> O (100:1)	80	24	82
15 <sup>f</sup>	1,4-Dioxane/H <sub>2</sub> O (100:1)	80	24	30

<sup>a</sup> All of reactions were carried out with phenylboronic acid (1 mmol), *p*-chlorobenzaldehyde (0.5 mmol), KO<sup>t</sup>Bu (0.5 mmol), and catalyst **2** (0.35 mol% Rh).<sup>b</sup> Isolated yields were based on aldehydes.<sup>c</sup> Catalyst **2** (0.18 mol% Rh).<sup>d</sup> Catalyst **2** (1.06 mol% Rh).<sup>e</sup> [Rh(COD)Cl]<sub>2</sub> (0.18 mol% based on aldehyde) and 10 mg imidazolium-loaded polymeric support (**1**) were added instead of **2**.<sup>f</sup> [Rh(COD)Cl]<sub>2</sub> (0.18 mol% based on aldehyde) was added instead of **2**.

was the variety of solvent, the ratio of 1,4-dioxane to water (Table 3). High yield of secondary alcohol was obtained for the first run when the volume ratio of 1,4-dioxane to water was 100:1. However, the yield reduced to only about 25% in the second run, suggesting the catalyst is unstable in this solvent. With the increasing of water content in the mixture solvent, the catalyst stability increased, but catalytic activity decreased markedly. The balance between activity and stability reached when the volume ratio of 1,4-dioxane to water was 4:1. After simple filtration and washing, the

recovered polymer-supported NHC–Rh catalyst was reused 6 times under the same reaction conditions as for the first run and still remained good activity.

Table 4 summarizes the addition of other arylboronic acids to various aldehydes catalyzed by polymer-supported NHC–Rh complex (**2**). The results reveal the wide scope of this method that is compatible with nitro, cyano, chloro and ether groups in aldehydes. Aldehydes with an electron-withdrawing group such as chloro, nitro, cyano reacted with arylboronic acids cleanly in excellent yields.

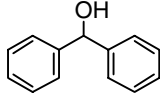
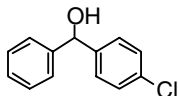
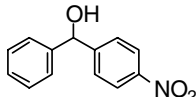
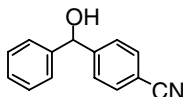
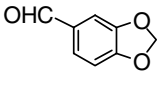
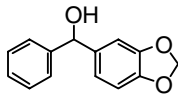
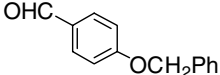
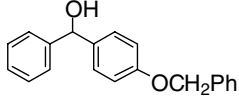
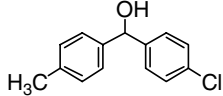
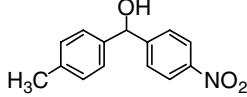
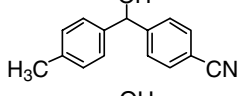
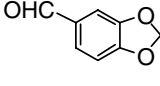
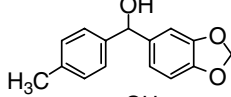
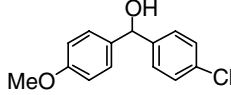
Table 3

Recycling of **2** in the addition of phenylboronic acid to *p*-chlorobenzaldehyde<sup>a</sup>

Entry	Dioxane/H <sub>2</sub> O (v/v)	Yield (%)					
		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
1	100:1	95	24.5	—	—	—	—
2	10:1	92	55	35.8	19.3	—	—
3	4:1	88	83	80	77	—	—
4 <sup>b</sup>	4:1	89	88	88	86	85	83
5	2:1	36	38	35	33	—	—

<sup>a</sup> All of reactions were carried out with phenylboronic acid (5.0 mmol), *p*-chlorobenzaldehyde (2.5 mmol), KO<sup>t</sup>Bu (2.5 mmol), catalyst **2** (0.35 mol% Rh) at 80 °C.<sup>b</sup> Catalyst **2** (1.0 mol% Rh) was used.

Table 4  
Rh-catalyzed addition of arylboronic acids to aldehydes<sup>a</sup>

Entry	Boronic acid	Aldehyde	Time (h)	Product	Yield (%) <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub> B(OH) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CHO	16		84
2		<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> CHO	24		89
3		<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> CHO	10		91
4		<i>p</i> -CN-C <sub>6</sub> H <sub>4</sub> CHO	6		94
5			40		83
6			30		85
7	<i>p</i> -Me-C <sub>6</sub> H <sub>4</sub> B(OH) <sub>2</sub>	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> CHO	24		92
8		<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> CHO	10		93
9		<i>p</i> -CN-C <sub>6</sub> H <sub>4</sub> CHO	6		95
10			36		86
11	<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> B(OH) <sub>2</sub>	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> CHO	6		95

<sup>a</sup> All of reactions were carried out with phenylboronic acid (1.0 mmol), aldehyde (0.5 mmol), Rh–NHC complex (**2**) (1.0 mol% Rh based on aldehyde), KO<sup>t</sup>Bu (0.5 mmol) in 1,4-dioxane/water (4:1, v:v), 80 °C. All reactions were monitored by TLC.

<sup>b</sup> Isolated yields were based on aldehyde.

Electron-donating group in aldehyde decreased the yield compared with the electron-withdrawing one (entries 5, 6 versus 2, 3, 4, Table 4).

### 3. Experimental

#### 3.1. General

Manipulations were performed using standard Schlenk techniques under an Ar atmosphere and with previously dried solvents. FT-IR spectra were recorded as KBr pellets

in the range 500–4000 cm<sup>−1</sup> on P-E FT-IR-16RC spectrometer. NMR spectra were recorded on a Varian INOVA 400 MHz or Bruker AC-E 200 MHz or Bruker Avance 600 MHz NMR spectrometer. Mass spectra experiments were conducted on Bruker Daltonics Data Analysis 3.2. Thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) were performed with Netzsch Sta 449C thermal analyzer. Nitrogen content was determined on Carlo Erba 1106 analyzer. Rhodium content was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on IRIS Adv.

### 3.2. Procedure for the preparation of imidazolium-loaded polymeric support (**1**)

Imidazolium-loaded polymeric support (**1**) was prepared from commercially available CM PS resin cross-linked with 1% DVB (100–200 mesh). A mixture of CM PS resin (1.0 g, 2.3 mmol Cl/g polymeric support) and (2,4,6-trimethylphenyl)imidazole (2.0 g, 10.7 mmol) in NMP (120 mL) was slowly agitated at 80 °C for 48 h. After cooling to room temperature, the reaction mixture was filtered, and the polymeric support was washed with NMP (20 mL  $\times$  3), 0.1 N aq. HCl (20 mL  $\times$  3), and methanol (20 mL  $\times$  3) followed by drying under reduced pressure to give **1**. The loading of the imidazolium was determined to be 0.61 mmol/g by means of the nitrogen content obtained from elementary analysis.

### 3.3. Procedure for measuring the swelling volumes of the imidazolium-loaded polymeric support (**1**)

The swelling volumes of the imidazolium-loaded polymeric support in various solvents were measured in a fritted column (ID 1.0 cm, length 10 cm). The polymeric support (1.0 g) was swollen in a solvent at room temperature for 4 h, and then washed with a 10-fold volume of each solvent. After filtering out the solvent, the volume of the polymeric support was measured.

### 3.4. Preparation of the polymer-supported NHC–Rh complex (**2**)

[Rh(COD)Cl]<sub>2</sub> (30 mg 0.12 mmol) was added to a Schlenk tube along with 3 equivalents of KO<sup>t</sup>Bu. The vessel was evacuated and flushed with Ar three times. THF (30 mL) was syringed in and stirred at room temperature for 2 h before the imidazolium-loaded polymeric support (**1**) (100 mg, 0.61 mmol/g) was added. The mixture was stirred at room temperature for 24 h. After filtration, the polymeric support was washed vigorously with THF (10 mL  $\times$  5) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL  $\times$  5) to give **2**. To measure the amount of Rh loaded on the polymeric support, the polymeric support (10 mg) was treated with a mixture (5 mL) of hydrochloric acid and nitric acid (1:1, v/v) at room temperature for 4 h. After the orange-colored solution was filtered, the polymeric support was washed with distilled water (2.5 mL  $\times$  2), and then, the filtrate and the washing solution were combined to determine the amount of Rh by ICP-AES. The loading level of immobilized rhodium was measured to be 0.18 mmol/g.

### 3.5. Rhodium-catalyzed addition of arylboronic acids to aldehydes

Arylboronic acid (1 mmol), KO<sup>t</sup>Bu (0.5 mmol), aldehyde (0.5 mmol), catalyst (**2**) (Rh 5  $\mu$ mol based on aldehyde) and 1,4-dioxane (5 mL) were introduced into a Schenk tube and then water (1.25 mL) was added. The resulting mixture was heated at 80 °C. After cooling to room temperature, the

reaction mixture was filtered, the polymeric support was washed vigorously with ether (10 mL  $\times$  3), and then, the filtrate and the washing solution were combined. The solvents were evaporated and the residue was purified by flash chromatography to give the corresponding alcohol.

4-(Phenylmethoxyl)diphenylmethanol: white solid, mp: 56–57 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.44–7.25 (m, 12H, phenyl-CH), 6.96–6.93 (m, 2H, phenyl-CH), 5.81 (s, 1H, CHOH), 5.06 (s, 2H, OCH<sub>2</sub>), 2.20 (s, br, 1H, OH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  158.2, 144.0, 136.9, 136.4, 128.5, 128.4, 127.9, 127.4, 127.3, 126.4, 114.8, 75.7, 70.0. HRMS (ESI):  $m/z$  calcd. for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub> [M+Na]<sup>+</sup>: 313.3515. Found 313.1199.

1,3-Benzodioxol-5-yl-4'-methyldiphenylmethanol: white solid, mp: 48–49 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.25–7.20 (m, 2H, phenyl-CH), 7.16–7.10 (m, 2H, phenyl-CH), 6.83–6.80 (m, 2H, phenyl-CH), 6.79–6.73 (m, 1H, phenyl-CH), 5.90 (m, 2H, OCH<sub>2</sub>O), 5.70 (s, 1H, CHOH), 2.32(s, 3H, CH<sub>3</sub>) 2.22 (s, br, 1H, OH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  147.6, 146.7, 140.9, 138.2, 137.0, 129.0, 126.2, 119.8, 107.9, 107.1, 100.8, 75.6, 21.0. MS (ESI):  $m/z$  265.1 [M+Na]<sup>+</sup>.

Other addition products, diphenylmethanol [11,39], 4-chlorodiphenylmethanol [39], 4-nitrodiphenylmethanol [40], 4-cyanodiphenylmethanol [11,41], 1,3-benzodioxol-5-yl-phenylmethanol [42], 4-chloro-4'-methyldiphenylmethanol [41], 4-methyl-4'-nitrodiphenylmethanol [43], 4-cyano-4'-methyldiphenylmethanol [41], 4-chloro-4'-methoxyldiphenylmethanol [44,45] have been identified by comparing their <sup>1</sup>H NMR spectra and melting points with that reported in the literature.

## 4. Conclusion

In summary, a novel polymer-supported NHC–Rh complex was prepared using a simple procedure. The polymer-supported NHC–Rh complex showed high catalytic activity in the addition of arylboronic acids to aldehydes giving diarylmethanols in satisfactory yields.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.02.021.

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