

# Synthesis of novel rhodium–carbene complexes as efficient catalysts for addition of phenylboronic acid to aldehydes

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## Abstract

Rhodium(I)–carbene complexes with 1,3-dialkylimidazolidin-2-ylidene ligand were prepared and characterized by conventional spectroscopic methods and elemental analyses. The rhodium–carbene complexes  $\text{RhCl}(\text{COD})(1,3\text{-dialkyl-imidazolinylidene})$ , **2a–d**, are an active catalyst for addition of phenylboronic acid to aldehydes.

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## 1. Introduction

In the last decade *N*-heterocyclic carbenes (NHC's) have been the subject of intense research in the field of organometallic chemistry [1,2]. Because of their extraordinary properties they have found access to a great variety of catalytic processes which include C–C-coupling reactions, [3] formation of furans, [4] cyclopropanation, [5] olefin metathesis, [6] hydroformylation, [7] polymerization [8] and hydrosilylation reactions [9].

Complexes containing imidazolin-2-ylidenes, which are neutral two-electron-donor ligands with negligible  $\pi$ -back-bonding, are thermally rather stable. This feature represents an essential prerequisite for the synthesis of highly efficient catalysts. The low reactivity of these ligands as compared to Fischer and Schrock type carbenes and to tertiary phosphines, which are susceptible to facile oxidation or P–C degradation makes them useful ancillary ligands to control the reactivity in a number of catalytic processes. Employment of sterically demanding *N*-heterocyclic carbenes, which resemble bulky phosphines with respect to their bonding, has led to the synthesis of new robust ruthenium,

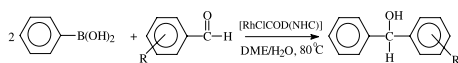
rhodium and palladium catalysts, which are less oxygen sensitive in comparison to the phosphine analogues [10].

Our contribution to this field has started with syntheses of imidazolidin-2-ylidenes complexes of Rh(I) and Ru(II) which are capable of catalyzing the cyclopropanation of styrene with ethyl diazoacetate and intramolecular cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran in good yields [4,5]. These complexes are insensitive to air and moisture and are thermally stable in both the solid state and in solution. We have now considered the possibility of generating heterocyclic carbenes that have pendent arene group to evaluate their ability to chelate the ruthenium atom, stabilise the complex or create catalytic activity [11].

Rhodium–carbene complexes have been extensively studied. However, there are few reports on the catalytic activity of rhodium–carbene complexes in rhodium-mediated processes [9,12]. Miyaura and co-workers [13] reported that rhodium catalyzes the addition of aryl and alkenylboronic acids to aldehydes giving secondary alcohols. The reactions were facilitated by the presence of an electron withdrawing group on the aldehyde and an electron donating group on the arylboronic acid, suggesting that the mechanism involves a nucleophilic attack of the aryl group on the aldehyde. The finding that these reactions were run with sterically hindered and strongly basic ligands attracted the attention of Fürstner who subsequently applied *N*-heterocyclic carbene ligands. A *in situ* generated catalytic system for the addition

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Scheme 1.

of phenylboronic acid to aldehydes is prepared combination of rhodium salt, 1,3-bis(alkyl or aryl)imidazolium chloride and base [14].

Based on these findings and our continuing interest in developing more efficient and stable catalysts, we wished to examine whether we could influence the catalytic activity of rhodium complexes for the addition of phenylboronic acid to aldehydes (Scheme 1).

We now report (i) the straightforward preparation of new  $\text{RhCl}(\text{COD})(1,3\text{-dialkyl-imidazolynilidene})$  complexes; (ii) their efficiency as catalysts for the addition of phenylboronic acid to aldehydes.

## 2. Experimental

Manipulations were prepared with standard Schlenk techniques under an inert atmosphere of nitrogen with previously dried solvents. The complex  $[\text{RhCl}(\text{COD})]_2$  [18] and 1,3-dialkyl-imidazolynilidene were prepared according to known methods [15]. Infrared spectra were recorded as KBr pellets in the range  $400\text{--}4000\text{ cm}^{-1}$  on a ATI UNICAM 2000 spectrometer.  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75.5 MHz) were recorded on a Bruker AM 300 WB FT spectrometer with chemical shifts referenced to residual solvent  $\text{CDCl}_3$ . Microanalyses were performed by the TÜBITAK analyses centre.

### 2.1. General procedure for the preparation of the rhodium–carbene complexes (2a–d)

A solution of 1,3-dialkyl-imidazolynilidene (**1**) (0.5 mmol) and  $[\text{RhCl}(\text{COD})]_2$  (0.5 mmol) in toluene (15 ml) was heated under reflux for 2 h. Upon cooling to room temperature, yellow-orange crystals of **2a–d** were obtained. The crystals were filtered, washed with diethyl ether ( $3 \times 15$  ml) and dried under vacuum.

### 2.2. General procedure for rhodium–carbene catalyzed addition of phenylboronic acid to aldehydes

Phenylboronic acid (1.20 g, 9.8 mmol),  $\text{KOtBu}$  (4.9 mmol), substituted aldehydes (4.9 mmol), rhodium carbene catalyst (1 mol%), dimethoxyethane (15 ml) were introduced in to Schlenk tube and then water (5 ml) was added. The resulting mixture was heated for 0.4–2.0 h at  $80^\circ\text{C}$ , cooled to ambient temperature, extracted with ethyl acetate (30 ml). After drying over  $\text{MgSO}_4$  the organic phase was evaporated and the residue was purified by flash chromatography (hexane/ethyl acetate, 6/1).

### 2.3. $\text{RhCl}(\text{COD})[\overline{\text{CN}\{\text{CH}_2\text{C}_6\text{H}_2\text{Me}_3-2,4,6\}\text{CH}_2\text{CH}_2\text{N}\{\text{CH}_2\text{C}_6\text{H}_2\text{Me}_3-2,4,6\}}]$ (**2a**)

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 2.83 [s, 4H,  $\text{NCH}_2\text{CH}_2\text{N}$ ]; 6.80 [s, 4H,  $\text{CH}_2\text{C}_6\text{H}_2\text{Me}_3-2,4,6$ ]; 5.00 and 3.60 [s, 4H,  $\text{CH}_2\text{C}_6\text{H}_2\text{Me}_3-2,4,6$ ]; 2.33 and 2.19 [s, 18H,  $\text{CH}_2\text{C}_6\text{H}_2\text{Me}_3-2,4,6$ ]; 5.50 and 5.03 [d,  $^3J = 13.90$  Hz, 4H,  $\text{CH}_{\text{COD}}$ ]; 2.37 and 1.9 [m, 8H,  $\text{CH}_2\text{COD}$ ];  $^{13}\text{C}$  {H}NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 214.6 [d,  $J = 46.58$  Hz,  $C_{\text{carbene}}$ ]; 47.7 [ $\text{NCH}_2\text{CH}_2\text{N}$ ]; 138.6, 138.0, 129.6 and 129.4 [ $\text{CH}_2\text{C}_6\text{H}_2\text{Me}_3-2,4,6$ ]; 49.1 [ $\text{CH}_2\text{C}_6\text{H}_2\text{Me}_3-2,4,6$ ]; 21.3 and 21.1 [ $\text{CH}_2\text{C}_6\text{H}_2\text{Me}_3-2,4,6$ ]; 99.5 and 68.0 [d,  $J = 6.64$  Hz and  $J = 14.65$  Hz,  $\text{CH}_{\text{COD}}$ ]; 33.3 and 29.1 [ $\text{CH}_2\text{COD}$ ]. Yield 0.540 g (93%).

Anal. cal. for  $\text{C}_{31}\text{H}_{42}\text{N}_2\text{ClRh}$ ; C: 64.08, H: 7.28, N: 4.82; found C: 64.11, H: 7.33, N: 4.86.

### 2.4. $\text{RhCl}(\text{COD})[\overline{\text{CN}\{\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5\}\text{CH}_2\text{CH}_2\text{N}\{\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5\}}]$ (**2b**)

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 3.24 [s, 4H,  $\text{NCH}_2\text{CH}_2\text{N}$ ]; 6.79 [s, 4H,  $\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5$ ]; 4.98 and 3.37 [s, 4H,  $\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5$ ]; 3.82 and 3.77 [s, 18H,  $\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5$ ]; 5.97 and 4.55 [d,  $^3J = 14.22$  Hz, 4H,  $\text{CH}_{\text{COD}}$ ]; 2.32 and 1.89 [m, 8H,  $\text{CH}_2\text{COD}$ ];  $^{13}\text{C}$  {H}NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 213.7 [d,  $J = 47.3$  Hz,  $C_{\text{carbene}}$ ]; 48.3 [ $\text{NCH}_2\text{CH}_2\text{N}$ ]; 154.8, 138.7, 133.1 and 106.7 [ $\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5$ ]; 61.6 [ $\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5$ ]; 57.2 and 55.6 [ $\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5$ ]; 100.5 and 69.4 [d,  $J = 6.40$  Hz and  $J = 14.40$  Hz,  $\text{CH}_{\text{COD}}$ ]; 33.5 and 29.3 [ $\text{CH}_2\text{COD}$ ]. Yield 0.602 g (89%).

Anal. cal. for  $\text{C}_{31}\text{H}_{42}\text{N}_2\text{O}_6\text{ClRh}$ ; C: 54.99, H: 6.25, N: 4.14; found C: 55.03, H: 6.24, N: 4.16.

### 2.5. $\text{RhCl}(\text{COD})[\overline{\text{CN}\{\text{C}_5\text{H}_9\}\text{CH}_2\text{CH}_2\text{N}\{\text{C}_5\text{H}_9\}}]$ (**2c**)

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 3.4 [m, 4H,  $\text{NCH}_2\text{CH}_2\text{N}$ ]; 4.9 [s, 2H,  $\text{CH}_{\text{Cp}}$ ]; 1.8 [m, 24H,  $\text{CH}_2\text{Cp}$  and  $\text{COD}$ ]; 5.7 and 5.6 [d,  $^3J = 8.0$  Hz, 4H,  $\text{CH}_{\text{COD}}$ ];  $^{13}\text{C}$  {H}NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 211.1 [d,  $J = 46.5$  Hz,  $C_{\text{carbene}}$ ]; 42.9 [ $\text{NCH}_2\text{CH}_2\text{N}$ ]; 61.4 [ $\text{CH}_{\text{Cp}}$ ]; 29.2, 28.9, 24.9 and 24.6 [ $\text{CH}_2\text{Cp}$ ]; 98.4 and 68.2 [d,  $J = 6.9$  Hz and  $J = 14.6$  Hz,  $\text{CH}_{\text{COD}}$ ]; 33.3 and 29.9 [ $\text{CH}_2\text{COD}$ ]. Yield 0.390 g (86%).

Anal. cal. for  $\text{C}_{21}\text{H}_{35}\text{N}_2\text{ClRh}$ ; C: 55.57, H: 7.77, N: 6.17; found C: 55.61, H: 7.74, N: 6.19.

### 2.6. $\text{RhCl}(\text{COD})[\overline{\text{CN}\{\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5\}\text{CH}_2\text{CH}_2\text{N}\{\text{CH}_2\text{CH}_2\text{OMe}\}}]$ (**2d**)

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 4.12 and 3.41 [s, 4H,  $\text{NCH}_2\text{CH}_2\text{N}$ ]; 6.75 [s, 2H,  $\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5$ ]; 4.92 [s, 2H,  $\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5$ ]; 3.83 and 3.77 [s, 9H,  $\text{CH}_2\text{C}_6\text{H}_2(\text{OMe})_3-3,4,5$ ]; 3.69 [m, 2H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ]; 4.47 [m, 2H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ]; 3.33 [m, 2H,  $\text{CH}_2\text{CH}_2\text{OCH}_3$ ]; 5.90 and 4.53 [d,  $^3J = 7.2$  Hz, 4H,  $\text{CH}_{\text{COD}}$ ]; 2.29 and 1.85 [m,

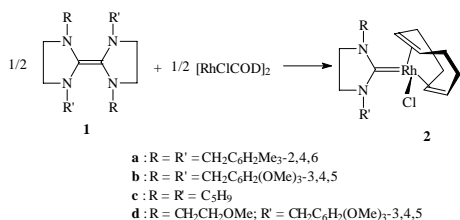
8H, CH<sub>2</sub>COD]; <sup>13</sup>C {H}NMR (δ, CDCl<sub>3</sub>): 213.2 [d, *J* = 46.7 Hz, C<sub>carbene</sub>]; 50.71 and 48.08 [NCH<sub>2</sub>CH<sub>2</sub>N]; 153.9, 137.8, 132.4 and 106.1 [CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-3,4,5]; 61.24 [CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-3,4,5]; 57.0 and 55.3 [CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-3,4,5]; 68.7 [CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>], 72.5 [CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]; 59.3 [CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]; 99.6 and 69.1 [d, *J* = 7.85 Hz and *J* = 10.85 Hz, CH<sub>2</sub>COD]; 33.3 and 29.2 [CH<sub>2</sub>COD]. Yield 0.499 g (90%).

Anal. cal. for C<sub>24</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>ClRh; C: 51.95, H: 6.54, N: 5.05; found C: 51.96, H: 6.55, N: 5.10.

### 3. Results and discussion

The tetraaminoethene, **1**, was synthesised using a method similar to that reported by Çetinkaya et al. [15]. The reaction of tetraaminoethene **1** with the binuclear [RhCl(COD)]<sub>2</sub> complex proceeded smoothly in refluxing toluene to give the RhCl(COD)(1,3-dialkyl-imidazolinyldene) complexes **2a–d** as crystalline solids in 86–93% yields (Scheme 2, Table 1).

Complexes **2a–d**, which are very stable in the solid state have been characterized by analytical and spectroscopic techniques (Table 1). Rhodium complexes exhibit a characteristic ν<sub>(NCN)</sub> band (Table 1) typically at 1590–1612 cm<sup>-1</sup> [5,16]. <sup>13</sup>C chemical shifts, which provide a useful diagnostic tool for metal–carbene complexes, show that C<sub>carb</sub> is substantially deshielded. Values of δ(<sup>13</sup>C<sub>carb</sub>) are in the range 211–214 ppm and are similar to those found in other carbene complexes. Coupling constants *J*(<sup>103</sup>Rh–<sup>13</sup>C) for the new rhodium complexes (**2a–d**) are comparable with those found for carbene rhodium(I) complexes (Table 1). These new complexes show typical spectroscopic signatures which are in line with those recently reported for other RhCl(COD)(1,3-dialkyl-imidazolinyldene) complexes [5,16,17].



Scheme 2.

Table 1  
Selected analytical data for the new rhodium–carbene complexes (**2a–d**)

Complex	Isolated yield (%)	mp (°C)	ν <sub>(NCN)</sub> (cm <sup>-1</sup> )	<sup>13</sup> C NMR Rh-C δ ppm ( <sup>1</sup> J <sub>Rh-C</sub> )
<b>2a</b>	93	235.0–235.5	1612	214.6 (46.6 Hz)
<b>2b</b>	89	218.0–219.0	1592	213.7 (47.3 Hz)
<b>2c</b>	86	221.5–222.0	1590	211.1 (46.5 Hz)
<b>2d</b>	90	152.5–153.0	1593	213.2 (46.7 Hz)

Table 2  
Rhodium–carbene catalyzed addition of phenylboronic acid to aldehydes

Entry	Catalyst	R	Time (h)	Yield (%) <sup>a,b,c</sup>
1	<b>2a</b>	<i>p</i> -OCH <sub>3</sub>	0.5	91
2	<b>2b</b>	<i>p</i> -OCH <sub>3</sub>	0.5	89
3	<b>2c</b>	<i>p</i> -OCH <sub>3</sub>	1.5	85
4	<b>2d</b>	<i>p</i> -OCH <sub>3</sub>	0.4	96
5	<b>2a</b>	<i>p</i> -OCH <sub>3</sub>	1.0	75 <sup>d</sup>
6	<b>2a</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub>	0.5	95
7	<b>2b</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub>	0.5	97
8	<b>2c</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub>	2.0	82
9	<b>2d</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub>	0.5	94
10	<b>2a</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub>	1.0	73 <sup>d</sup>
11	<b>2a</b>	3,4,5-(OCH <sub>3</sub> ) <sub>3</sub>	0.5	91
12	<b>2b</b>	3,4,5-(OCH <sub>3</sub> ) <sub>3</sub>	0.5	93
13	<b>2c</b>	3,4,5-(OCH <sub>3</sub> ) <sub>3</sub>	1.5	81
14	<b>2d</b>	3,4,5-(OCH <sub>3</sub> ) <sub>3</sub>	0.5	90
15	<b>2a</b>	3,4,5-(OCH <sub>3</sub> ) <sub>3</sub>	2.0	77 <sup>d</sup>
16	<b>2a</b>	<i>p</i> -Cl	0.5	91
17	<b>2b</b>	<i>p</i> -Cl	1.0	86
18	<b>2c</b>	<i>p</i> -Cl	2.0	74
19	<b>2d</b>	<i>p</i> -Cl	0.5	89
20	<b>2a</b>	<i>p</i> -Cl	2.0	71 <sup>d</sup>

<sup>a</sup> Isolated yield (purity of yield checked by NMR).

<sup>b</sup> Yields base on the aldehydes.

<sup>c</sup> All reactions were monitored by TLC.

<sup>d</sup> Base K<sub>2</sub>CO<sub>3</sub>.

Although the addition of carbon nucleophiles to aldehydes is usually a facile process, limits are encountered that functionalized organometallic reagents required. Rhodium complexes **2a–d** were found to be active catalysts for the addition of phenylboronic acid to aldehydes and proved to be thermally robust for high temperature. The addition of phenylboronic acid to aldehydes proceeds in high yields and quite rapidly even with a low catalyst loading. The results were summarized in Table 2. Under those conditions, 4-methoxybenzaldehyde, 2,4,6-trimethylbenzaldehyde, 3,4,5-trimethoxybenzaldehyde and 4-chlorobenzaldehyde react very cleanly with phenylboronic acid in goods yields (Table 2, entries 4, 7, 12 and 16).

### 4. Conclusion

From readily available starting materials, such as 1,3-dialkyl-imidazolinyldene four rhodium–carbene (**2a–d**) have been prepared and characterized. Also a convenient and highly user-friendly method for the addition of phenylboronic acid to aldehydes is presented. The procedure is simple and efficient towards various aryl aldehydes and does not require induction periods.

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