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# Novel rhodium *N*-heterocyclic carbene catalysed arylation of aldehydes with phenylboronic acid

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**Abstract**

Reaction of 1,3-dialkylperhydrobenzimidazolinylidene, 1,3-dialkyl-4-methylimidazolinylidene and 1,3-dialkylimidazolinylidene with $[RhCl(COD)]_2$ yields {1,3-dialkylperhydrobenzimidazolin-2-ylidene}-, {1,3-dialkyl-4-methylimidazolin-2-ylidene}- {1,3-dialkylimidazolin-2-ylidene}chloro($\eta^4$-1,5-cyclooctadiene)rhodium(I) complexes *(2a–c)* and *(4a, b)*. All compounds synthesised were characterised by elemental analysis, n.m.r. spectroscopy. Phenylboronic acid reacts with aldehydes in the presence of a catalytic amount of the new rhodium(I)–carbene complexes *(2a–c)* and *(4a, b)*, to give the corresponding aryl secondary alcohols in good yield (73–99%).

## Introduction

Specifically designed catalysts have been shown to play a key role in optimizing the efficiency of a wide variety of organic transformations. During the past few decades small molecule synthesis has attracted attention owing to its importance in the synthesis of key intermediates or compounds in pharmaceutical, agrochemical, and fine chemical industries. However, homogeneous catalysts are far from being widely used in industrial processes, mainly due to their low chemical and thermal stability and to their low potential to provide recyclable systems. With this in mind, recent research in this area has focused mainly on the search for new methods for the synthesis of stable, effective and recyclable catalysts, since this would combine both economic and environmental benefit.

Over the years the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of a variety of metal-containing systems. Advances in ligand design have allowed not only for improvements of known processes in terms of scope, mildness, and catalyst loadings, but also for the discovery of new selective reactions. Coordination chemistry directed towards catalysis has been boosted in recent years by the discovery of *N*-heterocyclic carbenes (NHCs) being powerful ligands [1].

Since the synthesis and isolation of the first stable *N*-heterocyclic carbene (NHC) by Arduengo *et al.* [2] these species have emerged over the past decade as a group of efficient ligands for transition metal-based homogeneous catalysts. In some aspects these compounds can be viewed as phosphane surrogates [3], the $\sigma$-donor ability of NHC ligands matching or improving that of the most basic phosphines. Additionally, NHC-based catalysts feature robust carbon-metal bonds that provide high thermal stability low dissociation rates, and consequently better resistance against oxidation or leaching phenomena, making the use of ligand excess unnecessary [4]. These properties have led to a number of applications where NHC-based catalysts exhibit superior performance. Such NHC–metal complexes have been successfully utilized in cross-coupling reactions [5] an related processes, including hydrogenation [5], hydroformylation [7], hydrosilylation [8], oxidation [9], metathesis [10], cycloisomerisation of olefins [11], the synthesis of furans [12] and for cyclopropanation reactions [13].

We have previously reported the use of an *in situ* formed imidazolidin-2-ylidene, tetrahydropyrimidin-2-ylidene and tetrahydrodiazepin-2-ylidenepalladium(II) system which exhibits high activity in various coupling reactions of aryl bromides and aryl chlorides. In order to obtain a more stable, efficient and active system, we have also investigated benzo-annelated derivatives [14].

The addition of organometallic reagents to aldehydes has been the general method for the synthesis of secondary alcohols. Among these reagents, organolithium and organomagnesium compounds are recognized to be the most versatile. However, limitations to their use arise from the very nature of the reagents, namely their extraordinary reactivity as nucleophiles and bases. This feature often gives rise to undesired

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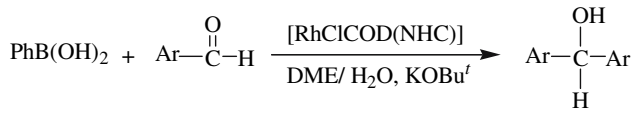
reactions in the synthesis of multifunctional compounds such as natural products. In order to realize chemoselective addition to aldehydes, various organometallic reagents have been investigated [15, 16].

Rhodium–carbene complexes have been extensively studied. However, there are few reports on the catalytic activity of rhodium–carbene complexes in rhodium-mediated processes [17, 18]. Miyaura 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 [19]. 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. An *in situ* generated catalytic system for the addition of phenylboronic acid to aldehydes is the prepared combination of rhodium salt, 1,3-dialkylimidazolium chloride and base [20].

Although the nature of the NHC ligand on complexes has a tremendous influence on the rate of catalyzed reactions, the use of saturated NHC ligands in the addition of phenylboronic acid to aldehydes reaction is a neglected area. In order to find more efficient rhodium catalysts we have prepared a series of new rhodium–NHC *(2a–c)* and *(4a, b)* complexes, containing a saturated imidazole ring and we report here a rhodium–carbene based catalytic system for the addition of phenylboronic acid to aldehydes (Scheme 1).




*Scheme 1.*

## Experimental

All reactions for the preparation of *(1–2)* were carried out under Ar in flame-dried glassware using standard Schlenk-type flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, $Et_2O$ (Na/K alloy), $CH_2Cl_2$ ($P_4O_{10}$), hexane, toluene (Na). Flash chromatography: Merck silica gel 60 (230–400 mesh). The complex $[RhCl(COD)]_2$ [21] and *(1)* and *(3)* were prepared according to known methods [22]. All reagents were purchased from Aldrich Chemical Co. All $^1$H- and $^{13}$C-n.m.r. were performed in $CDCl_3$. $^1$H-n.m.r. and $^{13}$C-n.m.r. spectra were recorded using a Varian A 400 Merkur spectrometer operating at 400 MHz ($^1$H-), 100 MHz ($^{13}$C-). Chemical shifts ($\delta$) are given in p.p.m. relative to TMS, coupling constants ($J$) in Hz. Infrared spectra were recorded as KBr pellets in the range 400–4000 $cm^{-1}$ on an ATI UNICAM 1000 spectrometer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. Elemental analyses were performed by Turkish Research Council (Ankara, Turkey) Microlab.

*General procedure for the preparation of the rhodium–carbene complexes (2a–c, 4a–b)*

A solution of 1,3-dialkyl-perhydrobenzimidazolinylidene *(1)* or 1,3-dialkyl-4-methylimidazolinylidene and 1,3-dialkyl-imidazolinylidene *(3)* (0.40 mmol) and $[RhCI(COD)]_2$ (0.40 mmol) in toluene (15 $cm^3$) was heated under reflux for 2 h. Upon cooling to room temperature , yellow-orange crystals of *(2a–c), (4a–b)* were obtained. The crystals were filtered, washed with diethyl ether (3 × 15 $cm^3$) and dried under vacuum. The crude product was recrystallized from $CH_2Cl_2$/$Et_2O$.

*Chloro($\eta^4$-1,5-cyclooctadiene){1,3-bis(4-methoxybenzyl)perhydrobenzimidazolin-2-ylidene}rhodium(I), (2a)*

Yield: 0.42 g, 88%, m.p. 200 °C. I.r., $\nu_{(NCN)}$: 1514 $cm^{-1}$. (Found: C, 60.9; H, 6.4; N, 4.65. $C_{31}H_{40}N_2O_2ClRh$ calcd.: C, 60.9; H, 6.55; N, 4.6%). $^1$H-n.m.r.($CDCl_3$): $\delta$ 0.97, 1.56 and 2.91 (m, 10H, NC*H*($CH_2$)$_4$C*H*N); 6.88 and 7.42 (d, 8H, $J$ = 8.0 Hz, $CH_2C_6H_4$OMe-*p*); 4.76, 6.14 and 5.14, 5.74 (d, 4H, $J$ = 14.8 Hz and $J$ = 15.2 Hz, $CH_2C_6H_4$OMe-*p*); 3.79 and 3.80 (s, 6H, $CH_2C_6H_4O$*Me-p*); 3.40 and 5.01 (m, 4H, $CH_{COD}$); 1.85 and 2.28 (m, 8H, $CH_{2COD}$). $^{13}$C-n.m.r. ($CDCl_3$): $\delta$ 219.49 (d, $J$ = 47.3 Hz, $C_{carbene}$); 24.11; 24.37; 28.74; 28.84; 53.60 and 53.87 (N*C*H($CH_2$)$_4$*C*HN); 114.02; 114.12; 128.88; 129.24; 129.49; 129.54; 130.20; 159.16 and 159.23 ($CH_2C_6H_4$OMe-*p*); 67.86 and 68.01 ($CH_2C_6H_4$OMe-*p*); 55.47 ($CH_2C_6H_4O$*Me-p*); 69.23 and 99.85 (d, $J$ = 14.5 Hz and $J$ = 6.1 Hz, $CH_{COD}$); 29.41, 29.46, 32.85 and 33.09 ($CH_{2COD}$).

*Chloro($\eta^4$-1,5-cyclooctadiene){1,3-bis(3,4,5-trimethoxybenzyl)perhydrobenzimidazolin-2-ylidene}rhodium(I), (2b)*

Yield: 0.48 g, 83%, m.p. 282 °C. I.r., $\nu_{(NCN)}$: 1508 $cm^{-1}$. (Found: C, 57.6; H, 6.5; N, 3.7. $C_{35}H_{48}N_2O_6ClRh$ calcd.: C, 57.5; H, 6.6; N, 3.8%). $^1$H-n.m.r. ($CDCl_3$): $\delta$ 0.99, 1.68 and 2.83 (m, 10H, NC*H*($CH_2$)$_4$C*H*N); 6.83 and 6.90 (s, 4H, $CH_2C_6H_4$(OMe)$_3$-3,4,5); 4.26; 5.06 and 5.82; 6.59 (d, 4H, $J$ = 14.8 Hz, $CH_2C_6H_4$(OMe)$_3$-3,4,5); 3.81; 3.83; 3.86 and 3.88 (s, 18H, $CH_2C_6H_4$(O*Me*)$_3$-3,4,5); 3.35 and 4.98 (m, 4H, $CH_{COD}$); 1.88 and 2.43 (m, 8H, $CH_{2COD}$). $^{13}$C-n.m.r. ($CDCl_3$): $\delta$ 219.48 (d, $J$ = 47.2 Hz, $C_{carbene}$); 23.98; 24.38; 28.58; 28.99; 53.85 and 54.75 (N*C*H($CH_2$)$_4$*C*HN); 105.71; 105.89; 131.90; 134.30; 137.57; 137.66; 153.39 and 153.63 ($CH_2C_6H_4$(OMe)$_3$-3,4,5); 66.77 and 68.12 ($CH_2C_6H_4$(OMe)$_3$-3,4,5); 56.66

and 56.86 [$CH_2C_6H_4(OMe)_3$-3,4,5]; 68.27 and 100.24 [d, $J$ = 14.5 Hz and $J$ = 6.1 Hz, $CH_{COD}$]; 29.11, 29.75, 32.66 and 33.33 ($CH_{2COD}$).

*Chloro($\eta^4$-1,5-cyclooctadiene){1,3-bis(2,4,5-trimethoxybenzyl)perhydrobenzimidazolin-2-ylidene}rhodium(I), (2c)*

Yield: 0.47 g, 81%, m.p. 206 °C. I.r., $\nu_{(NCN)}$: 1518 $cm^{-1}$. (Found: C, 57.4; H. 6.65; N, 3.9; $C_{35}H_{48}N_2O_6ClRh$ calcd.: C, 57.5; H, 6.6; N, 3.8%). $^1$H-n.m.r. ($CDCl_3$): $\delta$ 0.88; 1.49 and 2.72 (m, 10H, $NCH(CH_2)_4CHN$); 6.46; 6.50; 7.42 and 7.65 (s, 4H, $CH_2C_6H_4(OMe)_3$-2,4,5); 4.73; 5.37 and 5.62; 6.22 (d, 4H, $J$ = 14.8 Hz, $CH_2C_6H_4(OMe)_3$-2,4,5); 3.82; 3.83; 3.86; 3.87 and 3.88 (s, 18H, $CH_2C_6H_4(OMe)_3$-2,4,5); 3.36 and 4.97 (m, 4H, $CH_{COD}$); 1.88 and 2.34 (m, 8H, $CH_{2COD}$). $^{13}$C-n.m.r.($CDCl_3$): $\delta$ 218.39 (d, $J$ = 47.2 Hz, $C_{carbene}$); 24.11; 24.43; 28.58; 28.66; 45.73 and 46.36 ($NCH(CH_2)_4CHN$); 114.14; 114.57; 115.90; 118.61; 143.85; 143.92; 148.85; 149.08; 150.44 and 151.45 ($CH_2C_6H_4(OMe)_3$-2,4,5); 66.55 and 68.14 ($CH_2C_6H_4(OMe)_3$-2,4,5); 56.34; 56.39; 56.75; 56.82; 57.15 and 57.60 ($CH_2C_6H_4(OMe)_3$-2,4,5); 69.19 and 99.65 (d, $J$ = 14.5 Hz and $J$ = 6.9 Hz, $CH_{COD}$); 29.05; 29.19; 32.62 and 33.38 ($CH_{2COD}$).

*Chloro($\eta^4$-1,5-cyclooctadiene){1,3-bis(2,4,6-trimethylbenzyl)-4-methylimidazolin-2-ylidene}rhodium(I), (4a)*

Yield: 0.40 g, 86%, m.p. 218 °C. I.r., $\nu_{(NCN)}$: 1435 $cm^{-1}$. (Found: C, 64.5; H, 7.5; N, 4.8. $C_{32}H_{44}N_2ClRh$ calcd.: C, 64.6; H, 7.4; N, 4.7%). $^1$H-n.m.r. ($CDCl_3$): $\delta$ 3.34 (m, 1H, $NCH(CH_3)CH_2N$); 3.06 and 3.21 (t, 2H, $J$ = 9.2 Hz, $NCH(CH_3)CH_2N$); 0.78 (d, 3H, $J$ = 6.4 Hz, $NCH(CH_3)CH_2N$); 6.83; 6.85 and 6.86 (s, $CH_2C_6H_2Me_3$-2,4,6); 5.01; 5.46 and 5.23; 5.90 (d, 4H, $J$ = 14 Hz and $J$ = 14.4, $CH_2C_6H_2Me_3$-2,4,6); 2.24; 2.26; 2.39 and 2.42 (s, 18H, $CH_2C_6H_2Me_3$-2,4,6); 3.54 and 5.05 (m, 4H, $CH_{COD}$); 1.98 and 2.48 (m, 8H, $CH_{2COD}$). $^{13}$C-n.m.r. ($CDCl_3$): $\delta$ 214.05 (d, $J$ = 46.5 Hz, $C_{carbene}$); 19.67; 53.46 and 55.52 ($NCH(CH_3)CH_2N$); 128.59; 129.24; 129.34; 129.45; 129.64; 129.77; 137.50; 137.75; 137.84; 138.12; 138.38 and 138.51 ($CH_2C_6H_2Me_3$-2,4,6); 54.78 and 54.93 ($CH_2C_6H_2Me_3$-2,4,6); 20.18; 20.77; 20.91; 21.06; 21.09 and 21.13 ($CH_2C_6H_2Me_3$-2,4,6) 68.34 and 99.68 (d, $J$ = 14.5 Hz and $J$ = 6.1 Hz, $CH_{COD}$); 28.71; 28.99; 32.98 and 33.14 ($CH_{2COD}$).

*Chloro($\eta^4$-1,5-cyclooctadiene){1,3-bis(4-methoxybenzyl)imidazolin-2-ylidene}rhodium(I), (4b)*

Yield: 0.41 g, 92%, m.p. 217 °C. I.r., $\eta_{(NCN)}$: 1511 $cm^{-1}$. (Found: C, 58.6; H, 6.2; N, 5.2. $C_{27}H_{34}N_2O_2ClRh$ calcd.: C, 58.5; H, 6.1; N, 5.3%).$^1$H-n.m.r.($CDCl_3$): $\delta$ 3.24 (m, 4H, $NCH_2CH_2N$); 6.89 and 7.39 (d, 8H, $J$ = 8.4 Hz and $J$ = 8.8 Hz, $CH_2C_6H_4OMe$-*p*); 5.17 and 5.46 (d, 4H, $J$ = 14.4, $CH_2C_6H_4NMe_2$-*p*); 3.79 (s, 6H, $CH_2C_6H_4OMe$-*p*); 3.47 and 5.04 (m, 4H, $CH_{COD}$); 1.93 and 2.35 (m, 8H, $CH_{2COD}$). $^{13}$C-n.m.r.($CDCl_3$): $\delta$ 212.70 (d, $J$ = 47.3 Hz, $C_{carbene}$); 47.98 ($NCH_2CH_2N$); 114.37; 128.59; 129.88 and 159.49 ($CH_2C_6H_4OMe$-*p*); 54.54 ($CH_2C_6H_4OMe$-*p*); 55.51 ($CH_2C_6H_4OMe$-*p*); 68.63 and 99.55 (d, $J$ = 14.5 Hz and $J$ = 6.1 Hz, $CH_{COD}$); 28.92 and 33.07 ($CH_{2COD}$).

*General procedure for rhodium–carbene catalyzed addition of phenylboronic acid to aldehydes*

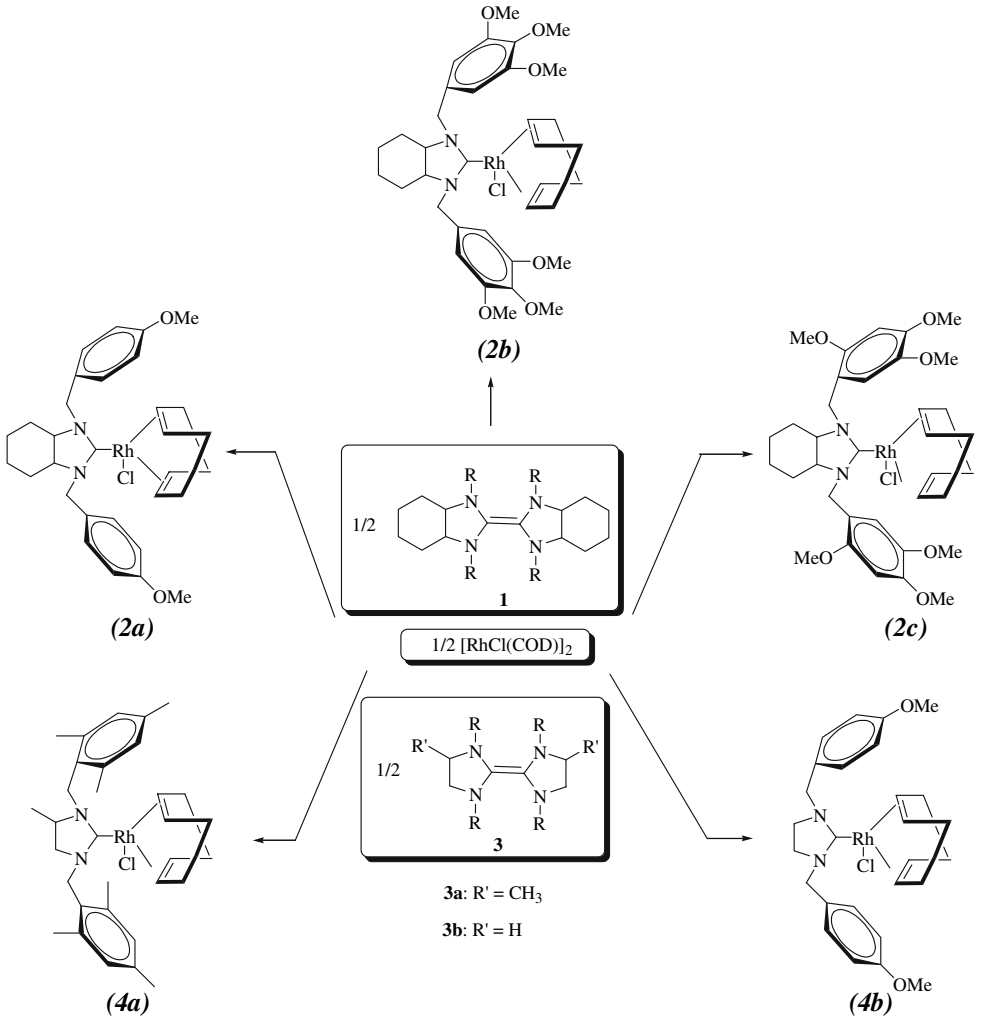
Phenylboronic acid (1.20 g, 9.8 mmol), $KOBu^t$ (4.9 mmol), substituted aldehydes (4.9 mmol), rhodium carbene catalyst (1 mol%), and dimethoxyethane (15 $cm^3$) were introduced into a Schlenk tube and then $H_2O$ (5 $cm^3$) was added. The resulting mixture was heated for 8 h at 80 °C, cooled to ambient temperature and extracted with ethyl acetate (30 $cm^3$). After drying over $MgSO_4$ the organic phase was evaporated and the residue was purified by flash chromatography (hexane/ethyl acetate, 6/1). Isolated yield (yields based on aldehydes) were checked by n.m.r. and GC, and all reactions were monitored by TLC.

## Results and discussion

The tetraaminoethenes, *(1)* and *(3)* were synthesised using a method similar to that reported by Lappert *et al.* [22]. The reaction of tetraaminoethene *(1)* and *(3)* with the binuclear $[RhCl(COD)]_2$ complex proceeded smoothly in refluxing toluene to give the $[RhC_2(NHC)(COD)]$ *(2a–c)* and *(4a, b)* complexes as crystalline solids in 81–92% yields (Scheme 2).

Each rhodium compound was fully characterized by $^1$H-n.m.r. and $^{13}$C-n.m.r spectroscopy, FT-IR, and elemental analysis. The rhodium complexes exhibit a characteristic $\upsilon_{(NCN)}$ band typically at 1435–1518 $cm^{-1}$ [23]. $^{13}$C-chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that $C_{carb}$ is substantially deshielded. Values of $\delta(^{13}C_{carb})$ are in the range 212.70–219.49 p.p.m. and are similar to those found in other carbene complexes. Coupling constants $J(^{103}Rh–^{13}C)$ for the new rhodium complexes *(2)* and *(4)* are comparable with those found for carbene rhodium(I) complexes. These new complexes show typical spectroscopic signatures which are in line with those recently reported for RhCl(COD)(1,3-dialkylimidazolin-2-ylidine) complexes [23].

Although the addition of carbon nucleophiles to aldehydes is usually a facile process, limits are encountered that functionalized organometallic reagents require. Recent publications describing the addition of arylboronic acid derivatives to aldehydes in the presence of the catalytic amounts of Rh(I) and phosphine derivatives deserve particular mention [19, 20]. Originally $[Rh(acac)(CO)_2]$ in combination with bidentate




*Scheme 2.* Synthesis of rhodium–carbene complexes (*2a–c*) and *4a,b*).

phosphine ligand such as dppf [1,1′-*bis*(diphenylphosphino)ferrocene] has been recommended for the *in situ* preparation of the yet elusive catalyst [24].

Here, various 1,3-dialkylperhydrobenzimidazolinylidene, 1,3-dialkyl-4-methylimidazolinylidene and 1,3-dialkylimidazolinylidene *(1)* and *(3)* were compared as ligand precursors under the same reaction conditions. To survey the reaction parameters for the addition of phenylboronic acid to aldehydes, we chose to examine $Cs_2CO_3$, $K_2CO_3$, and $KOBu^t$ as base and DME/$H_2O$ (3:1) as solvent. We found that the reactions performed in DME/$H_2O$ (3:1) with $Cs_2CO_3$ or $KOBu^t$ as the base at 80 °C appeared to be best. We started our investigation with the addition of phenylboronic acid to *p*-chlorobenzaldehyde, in the presence of $[RhCl(COD)]_2$/*(2)* and *(4)*. Table 1 summarizes the results obtained in the presence of *(2a–c)* and *(4a, b)* (Table 1 , entries 1–5).

Control experiment indicated that the addition of phenylboronic acid to *p*-chlorobenzaldehyde reaction did not occur in the absence of *(2a)*. Under the determined reaction conditions, a wide range of aryl aldehydes bearing electron-donating or electron-withdrawing groups can react with phenylboronic acid affording the addition products in excellent yields (Table 1 entries 2, 9, 13, 19, 24 and 29). A systematic study on the substituent effect in the imidazolidin-2-ylidene *(2)* and *(4)* indicated that the introduction of 2,4,6-trimethybenzyl substituent on the N-atoms notably increased the reaction rate and the yield of the product.

## Conclusion

From readily available starting materials, such as 1,3-dialkylperhydrobenzimidazolinylidene, 1,3-dialkyl-4-methylimidazolinylidene and 1,3-dialkylimidazolinylidene five rhodium–carbene *(2)* and *(4)* complexes have been prepared and characterized. We were pleased to find that among the various Rh–NHC complexes *(2, 4)* are excellent ligand precursors for the addition of phenylboronic acid to aldehydes reaction. 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. Detailed investigations, focusing on perhydrobenzimidazolinylidene, imidazolinylidene and

*Table 1.* Rhodium–carbene catalyzed addition of phenylboronic acid to aldehydes

| Entry | R | LHX | Yield %[a–d] |
|---|---|---|---|
| 1 | *p*-Cl | 2a | 85 |
| 2 | *p*-Cl | 2b | 95 |
| 3 | *p*-Cl | 2c | 75 |
| 4 | *p*-Cl | 4a | 73 |
| 5 | *p*-Cl | 4b | 85 |
| 6 | H | 2a | 96 |
| 7 | H | 2b | 70 |
| 8 | H | 2c | 72 |
| 9 | H | 4a | 99 |
| 10 | H | 4b | 98 |
| 11 | $2,4,6(CH_3)_3$ | 2a | 89 |
| 12 | $2,4,6(CH_3)_3$ | 2b | 93 |
| 13 | $2,4,6(CH_3)_3$ | 2c | 98 |
| 14 | $2,4,6(CH_3)_3$ | 4a | 90 |
| 15 | $2,4,6(CH_3)_3$ | 4b | 99 |
| 16 | $p$-$C(CH_3)_3$ | 2a | 86 |
| 17 | $p$-$C(CH_3)_3$ | 2b | 88 |
| 18 | $p$-$C(CH_3)_3$ | 2c | 78 |
| 19 | $p$-$C(CH_3)_3$ | 4a | 95 |
| 20 | $p$-$C(CH_3)_3$ | 4b | 97 |
| 21 | $2,5(OCH_3)_2$ | 2a | 96 |
| 22 | $2,5(OCH_3)_2$ | 2b | 78 |
| 23 | $2,5(OCH_3)_2$ | 2c | 87 |
| 24 | $2,5(OCH_3)_2$ | 4a | 99 |
| 25 | $2,5(OCH_3)_2$ | 4b | 98 |
| 26 | $3,4,5(OCH_3)_3$ | 2a | 98 |
| 27 | $3,4,5(OCH_3)_3$ | 2b | 84 |
| 28 | $3,4,5(OCH_3)_3$ | 2c | 93 |
| 29 | $3,4,5(OCH_3)_3$ | 4a | 99 |
| 30 | $3,4,5(OCH_3)_3$ | 4b | 88 |

[a]Isolated yield (purity of yield checked by n.m.r. and GC).
[b]Yields are based on aldehydes.
[c]All reactions were monitored by TLC.
[d]80 °C, 8 h.

substituent effects, functional group tolerance and catalytic activity in this and other addition reactions are ongoing.

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