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Novel rhodium-1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidene complexes as catalysts for arylation of aromatic aldehydes

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Abstract

Six new rhodium-tetrahydropyrimidin-2-ylidene complexes (**2a**–**f**) have been prepared and characterized by C, H, N analysis, ^{1}H NMR and ^{13}C NMR. Phenylboronic acid reacts with aldehydes in the presence of a catalytic amount of the new rhodium(I)-carbene complexes, RhCl(COD)(1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidene), (**2a**–**f**), to give the corresponding secondary aryl alcohols in good yields (72–96%).

Keywords: Tetrahydropyrimidin-2-ylidene; N-heterocyclic carbene; Arylation; Rhodium

1. Introduction

The first metal complexes of N-heterocyclic carbenes (NHCs) were reported independently in 1968 by Wanzlick [1] and Öfele [2] and subsequently, electron-rich alkenes were used as a source of various NHC complexes by Lappert and co-workers [3,4]. Since the 1991 isolation and crystallographic characterization of stable of N-heterocyclic carbenes by Arduengo [5], increasing attention has been focused on using these compounds as ancillary ligands for transition-metal complexes. Interestingly, most studies focusing on catalysts incorporating NHC ligands have revolved around the platinum metal groups. In numerous instances simple substitution reaction routes involving replacement of phosphines by NHC ligands lead to higher catalytic activity as well as improved thermal stability of the resulting organometallic complex. The working hypothesis is that NHCs are strong σ-donors with negligible π-accepting ability, and so they resemble donor phosphine ligands rather than classical Fischer- or Schrock-type carbenes [6] and thereby also lead to electron-rich metal centers [7]. However, in contrast to metal phosphine complexes, they can form metal complexes that have high stability towards heat, moisture, and oxygen [8].

The ancillary ligand (NHC) coordinated to the metal center has a number of important roles in homogeneous catalysis such as providing a stabilizing effect and governing activity and selectivity. The number, nature and position of the substituents on the nitrogen atom(s) and/or NHC ring have been found to play a crucial role in tuning the catalytic activity. Whilst many modifications to the five-membered ring of the ligand aryl substituent have been described, relatively little attention has been paid to the effect of the ring size [9]. For the present study, we selected 3,4,5,6-tetrahydropyrimidin-2-ylidene precursors (**2**). This choice was guided by several considerations. An important characteristic of the carbene ligands in active complexes is their strong-electron donating effect, primarily a σ-effect. We have previously reported the use of

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an in situ formed imidazolidin-2-ylidenepalladium(II) system which exhibits high activity in various coupling reactions of aryl bromides and aryl chlorides [10]. In order to obtain a more stable, efficient and active system, we have also investigated benzo-annelated derivatives [11]. Due to their six-membered ring geometry, tetrahydopyrimidine-2-ylidenes are stronger σ-donating ligands when compared to five-membered analogues [9].

Although, rhodium-carbene complexes have been extensively studied, there are few reports on the catalytic activity of rhodium-carbene complexes in rhodium-mediated processes [12,13]. Buchmeiser and Herrmann have addressed the synthesis and catalytic properties of 1,3-dimesityltetrahydropyrimidine-2-ylidene complexes of palladium and rhodium [14,15]. Miyaura reported that rhodium catalyse 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 [16]. 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 prepared by combination of rhodium salt, 1,3-dialkylimidazolium chloride and base [17]. Recently our group reported that novel complexes of rhodium(I) based on 1,3-dialkyimidazolidin-2-ylidenes give good yields for the addition of phenylboronic acid to aldehydes [18].

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-1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidene complexes for the addition of phenylboronic acid to aldehydes (Scheme 1).

We now report: (i) the straightforward preparation of new RhCl(COD)(1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidene) complexes and (ii) their efficient catalysis of the addition of phenylboronic acid to aldehydes.

2. Experimental

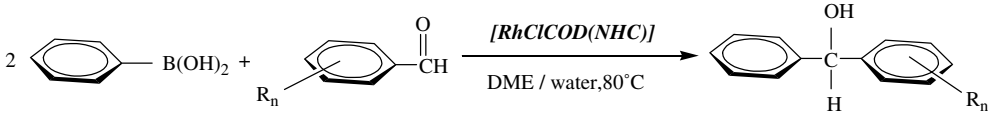
All reactions for the preparation of **1** and **2** were carried out under Ar in flame-dried glass-ware using standard Schlenk-type flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). Flash chromatography: Merck silica gel 60 (230–400 mesh). Test reactions for the catalytic activity of catalysts in the addition of phenylboronic acid to aldehydes were carried out in air. The complex $[RhCl(COD)]_2$[19] and **1** were prepared according to known methods [20]. All reagents were purchased from Aldrich Chemical Co. All ^1H and ^{13}C NMR were performed in $CDCl_3$. ^1H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 399.9 MHz (^1H), 100.5 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hertz. Infrared spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a 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 TUBITAK (Ankara, Turkey) Microlab.

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

A solution of bis(1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidene) (**1**) (0.5 mmol) and $[RhCl(COD)]_2$ (0.5 mmol) in toluene (20 mL) were heated under reflux for 2 h. Upon cooling to room temperature, yellow-orange crystals of **2a–f** were obtained. The crystals were filtered, washed with diethyl ether (3 × 15 mL) and dried under vacuum. The crude product was recrystallized from CH_2Cl_2/Et_2O.

2.2. Chloro(η^4-1,5-cyclooctadiene){1,3-bis(2,4,6-trimethylbenzyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene}-rhodium(I) (*2a*)

Yield: 0.517 g (87%). Anal. Calc. for $C_{32}H_{44}N_2ClRh$: C, 64.59; H, 7.45; N, 4.71. Found: C, 64.55; H, 7.47; N, 4.70%; m.p. 236–237 °C, $\nu_{(CN)} = 1619\ cm^{-1}$. ^1H NMR (399.9 MHz, $CDCl_3$) δ 6.86 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 6.62 and 5.33 (d, $J = 14.0$ Hz, 4H, CH_{COD}), 4.94 and 3.40 (m, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.62 (t, $J = 4.4$ Hz, 4H, $NCH_2CH_2CH_2N$), 2.51(m, 4H, CH_{2COD}), 2.40 (s, 12H, $CH_2C_6H_2(CH_3)_3$-2,6), 2.26 (s,



Scheme 1.

6H, $CH_2C_6H_2(CH_3)_3$-4), 1.93 (m, 4H, CH_{2COD}), 1.65 (quint, $J = 4.4$ Hz, 2H, $NCH_2CH_2CH_2N$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 211.9 (d, $J = 45.7$ Hz, $C_{carbene}$), 138.9, 137.7, 129.5 and 129.2, ($CH_2C_6H_2(CH_3)_3$-2,4,6), 97.0 and 69.6 (d, $J = 6.8$ Hz and $J = 15.3$ Hz, CH_{COD}), 55.4 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 43.1 ($NCH_2CH_2CH_2N$), 32.9 and 28.9 (CH_{2COD}), 22.1 ($NCH_2CH_2CH_2N$), 21.1 ($CH_2C_6H_2(CH_3)_3$-4), 21.0 ($CH_2C_6H_2(CH_3)_3$-2,6).

2.3. Chloro(η^4-1,5-cyclooctadiene){1,3-bis(3,4,5-trimethoxybenzyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene}rhodium(I) (**2b**)

Yield: 0.629 g (91%). Anal. Calc. for $C_{32}H_{44}N_2O_6ClRh$: C, 55.62; H, 6.42; N, 4.05. Found: C, 55.59; H, 6.45; N, 4.01%; m.p. 217–218 °C, $\nu_{(CN)} = 1592\ cm^{-1}$. ^1H NMR (399.9 MHz, $CDCl_3$) δ 6.91 (s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 6.83 (d, $J = 14.0$ Hz, 2H, CH_{COD}), 4.89 (m, 2H,$CH_2C_6H_2(OCH_3)_3$-3,4,5), 4.83 (d, $J = 14.0$ Hz, 2H, CH_{COD}), 3.88 (s, 12H, $CH_2C_6H_2(OCH_3)_3$-3,5), 3.83 (s, 6H, $CH_2C_6H_2(OCH_3)_3$-4), 3.36 (m, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 2.89 (t,$J = 5.6$ Hz, 4H, $NCH_2CH_2CH_2N$), 2.33 (m, 4H, CH_{2COD}), 1.87 (m, 4H, CH_{2COD}), 1.74 (quint, $J = 5.6$ Hz, 2H, $NCH_2CH_2CH_2N$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 206.9 (d, $J = 45.7$ Hz, $C_{carbene}$), 153.6, 137.7, 132.6 and 106.2 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 97.1 and 69.6 (d, $J = 6.9$ Hz and $J = 15.3$ Hz, CH_{COD}), 62.8 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 61.0 ($CH_2C_6H_2(OCH_3)_3$-4), 56.7 ($CH_2C_6H_2(OCH_3)_3$-3,5), 43.3 ($NCH_2CH_2CH_2N$), 32.8 and 29.0 (CH_{2COD}), 21.3 ($NCH_2CH_2CH_2N$).

2.4. Chloro(η^4-1,5-cyclooctadiene){1-(2,4,6-trimethylbenzyl)-3-cyclohexyl-3,4,5,6-tetrahydropyrimidin-2-ylidene}rhodium(I) (**2c**)

Yield: 0.457 g (84%). Anal. Calc. for $C_{28}H_{42}N_2ClRh$: C, 61.71; H, 7.77; N, 5.14. Found: C, 61.75; H, 7.78; N, 5.17%; m.p. 221–222 °C, $\nu_{(CN)} = 1510\ cm^{-1}$. ^1H NMR (399.9 MHz, $CDCl_3$) 6.86 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 5.91 and 5.41 (d, $J = 13.6$ Hz, 4H, CH_{COD}), 4.89 (m, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.46 (quint, $J = 7.2$ Hz, 1H, $NCH(CH_2)_4CH_2$), 3.37 and 2.97 (t,$J = 4.8$ Hz, 4H, $NCH_2CH_2CH_2N$), 2.36 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,6), 2.31 (m, 4H, CH_{2COD}), 2.27 (s, 3H, $CH_2C_6H_2(CH_3)_3$-4), 1.85 (m, 4H, CH_{2COD}), 1.75 (quint, $J = 4.8$ Hz, 2H, $NCH_2CH_2CH_2N$), 1.22 (m, 10H, $NCH(CH_2)_4CH_2$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 209.0 (d, $J = 45.8$ Hz, $C_{carbene}$), 139.0, 137.6, 129.4 and 129.3 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 95.8 and 68.2 (d, $J = 6.9$ Hz and $J = 9.2$ Hz, CH_{COD}), 66.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 54.7 ($NCH(CH_2)_4CH_2$), 43.1 and 39.3 ($NCH_2CH_2CH_2N$), 32.9 and 28.7 (CH_{2COD}), 26.6, 26.3 and 26.0 ($NCH(CH_2)_4CH_2$), 21.1 ($CH_2C_6H_2(CH_3)_3$-4), 20.9 ($CH_2C_6H_2(CH_3)_3$-2,6), 14.3 ($NCH_2CH_2CH_2N$).

2.5. Chloro(η^4-1,5-cyclooctadiene){1-methoxyethyl-3-(3,4,5-trimethoxybenzyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene}rhodium(I) (**2d**)

Yield: 0.489 g (86%). Anal. Calc. for $C_{25}H_{38}N_2O_4ClRh$: C, 52.78; H, 6.73; N, 4.92. Found: C, 52.75; H, 6.70; N, 4.93%; m.p. 219–220 °C, $\nu_{(CN)} = 1592\ cm^{-1}$. ^1H NMR (399.9 MHz, $CDCl_3$) δ 6.90 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 6.81 (d, $J = 14.0$ Hz, 2H, CH_{COD}), 4.88 (m, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 4.83 (d, $J = 14.0$ Hz, 2H, CH_{COD}), 3.91 (s, 3H, $CH_2CH_2OCH_3$), 3.87 (s, 6H, $CH_2C_6H_2(OCH_3)_3$-3,5), 3.83 (s, 3H, $CH_2C_6H_2(OCH_3)_3$-4), 3.35 and 3.17 (t, $J = 5.6$ Hz, 4H, $NCH_2CH_2CH_2N$), 2.89 (m, 4H, $CH_2CH_2OCH_3$), 2.32 and 1.87 (m, 8H, CH_{2COD}), 1.74 (quint, $J = 5.6$ Hz, 2H, $NCH_2CH_2CH_2N$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 206.9 (d, $J = 46.5$ Hz, $C_{carbene}$), 153.7, 137.7, 132.6 and 106.2 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 97.13 and 69.6 (d, $J = 6.9$ Hz and $J = 15.2$ Hz, CH_{COD}), 66.0 ($CH_2CH_2OCH_3$), 62.8 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 61.0 ($CH_2CH_2OCH_3$), 59.3 ($CH_2CH_2OCH_3$), 56.9 ($CH_2C_6H_2(OCH_3)_3$-4), 56.7 ($CH_2C_6H_2(OCH_3)_3$-3,5), 43.3 and 41.8 ($NCH_2CH_2CH_2N$), 32.9 and 29.0 (CH_{2COD}), 21.4 ($NCH_2CH_2CH_2N$).

2.6. Chloro(η^4-1,5-cyclooctadiene){1-(2,4,6-trimethylbenzyl)-3-methyl-3,4,5,6- tetrahydropyrimidin-2-ylidene}rhodium(I) (**2e**)

Yield: 0.405 g (85%). Anal. Calc. for $C_{23}H_{34}N_2ClRh$: C, 57.93; H, 7.19; N, 5.87. Found: C, 57.90; H, 7.21; N, 5.85%; m.p. 203–204 °C, $\nu_{(CN)} = 1535\ cm^{-1}$. ^1H NMR (399.9 MHz, $CDCl_3$) 6.87 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 5.94 and 5.40 (d, $J = 14.0$ Hz, 4H, CH_{COD}), 4.90 (m, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.96 (s, 3H, NCH_3), 3.13 and 3.06 (m, 4H, $NCH_2CH_2CH_2N$), 2.36 (m, 4H, CH_{2COD}), 2.32 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,6), 2.25 (s, 3H, $CH_2C_6H_2(CH_3)_3$-4), 1.84 (m, 4H, CH_{2COD}), 1.64 (quint, $J = 6.4$ Hz, 2H, $NCH_2CH_2CH_2N$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 209.5 (d, $J = 45.8$ Hz, $C_{carbene}$), 139.1, 137.8, 129.4 and 129.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 96.6 and 67.5 (d, $J = 6.1$ Hz and $J = 15.3$ Hz, CH_{COD}), 54.7 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 46.9 and 46.5 ($NCH_2CH_2CH_2N$), 41.2 (NCH_3), 32.2 and 28.3 (CH_{2COD}),21.1 ($CH_2C_6H_2(CH_3)_3$-4), 20.9 ($CH_2C_6H_2(CH_3)_3$-2,6), 15.5 ($NCH_2CH_2CH_2N$).

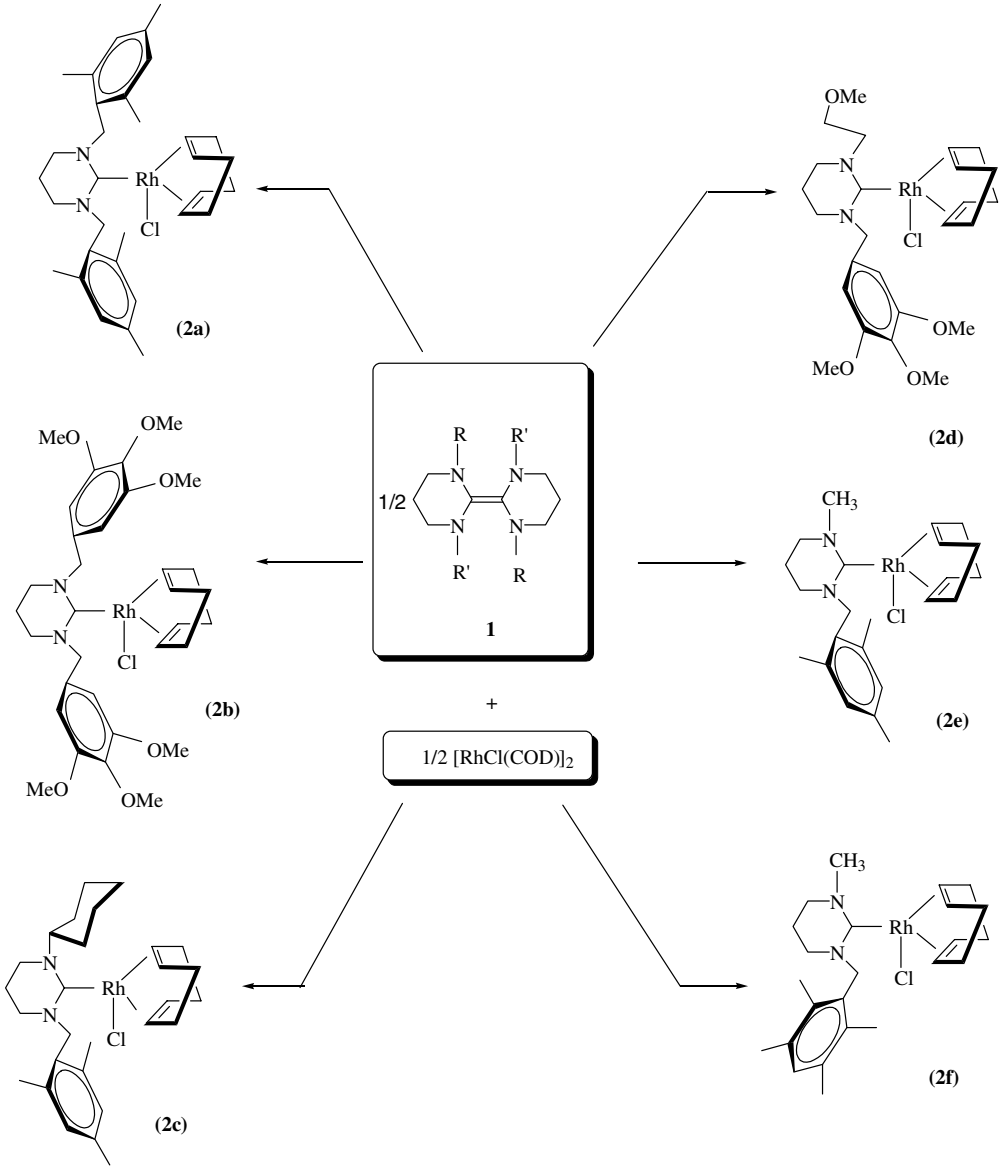
2.7. Chloro(η^4-1,5-cyclooctadiene){1-(2,3,5,6-tetramethylbenzyl)-3-methyl-(3,4,5,6-tetrahydropyrimidin)-2-ylidene}rhodium(I) (**2f**)

Yield: 0.397 g (81%). Anal. Calc. for $C_{24}H_{36}N_2ClRh$: C, 58.72; H, 7.39; N, 5.71. Found: C, 58.70; H, 7.41; N, 5.68%; m.p. 250–251 °C, $\nu_{(CN)} = 1536\ cm^{-1}$.$^1H$ NMR (399.9 MHz, $CDCl_3$) 6.96 (s, 1H, $CH_2C_6H(CH_3)_4$-

2,3,5,6), 5.97 and 5.47 (d, $J = 13.6$ Hz, 4H, CH_{COD}), 4.87 (m, 2H, CH_2C$_6$H(CH$_3$)$_4$-2,3,5,6), 3.96 (s, 3H, NCH_3), 3.36 and 3.10 (m, 4H, NCH_2CH$_2$CH_2N), 2.35 (m, 4H, CH_{2COD}), 2.27 (s, 6H, CH$_2$C$_6$H(CH_3)$_4$-2,6), 2.24 (s, 6H, CH$_2$C$_6$H(CH_3)$_4$-3,5), 1.96 (m, 4H, CH_{2COD}), 1.62 (quint, $J = 5.2$ Hz, 2H, NCH$_2$CH_2CH$_2$N). ^{13}C NMR (100.5 MHz, CDCl$_3$) δ 209.6 (d, $J = 45.8$ Hz, $C_{carbene}$), 135.3, 134.2, 132.1 and 131.8 (CH$_2$$C_6$H(CH$_3$)$_3$-2,3,5,6), 96.5 and 67.5 (d, $J = 6.9$ Hz and $J = 15.2$ Hz, CH$_{COD}$), 55.0 (CH$_2$C$_6$H(CH$_3$)$_4$-2,3,5,6), 47.0 and 46.6 (NCH$_2$-CH$_2$$CH_2$N), 41.3 (N$CH_3$), 32.2 and 28.3 ($CH_{2COD}$), 21.9 (CH$_2C_6$H($CH_3$)$_4$-3,5), 20.7 (CH$_2C_6$H($CH_3$)$_4$-2,6), 16.6 (NCH$_2$$CH_2CH_2$N).

2.8. General procedure for rhodium-carbene catalyzed addition of phenylboronic acid to aldehydes

Phenylboronic acid (1.20 g, 9.8 mmol), KO*t*Bu (4.9 mmol), substituted aldehydes (4.9 mmol), rhodium carbene catalyst (1 mmol%) and dimethoxyethane (15 mL) were introduced into a Schlenk tube and then water (5 mL) was added. The resulting mixture was heated for 4–10 h at 80 °C, cooled to ambient temperature and extracted with ethyl acetate (30 mL). After drying over $MgSO_4$ the organic phase was evaporated and the residue was purified by flash chromatography (hexane/ethyl acetate, 5/1).



Scheme 2. Synthesis of rhodium-carbene complexes (**2a**–**f**).

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

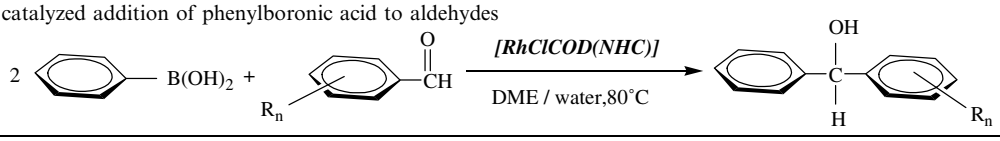
Complex	Isolated yield (%)	m.p. (°C)	$\nu_{(NCN)}(cm^{-1})$	^{13}C NMR Rh–C δ ppm (^{1}J(Rh–C), Hz)
2a	87	236–237	1619	211.9 (45.7)
2b	91	217–218	1592	196.9 (45.7)
2c	84	221–222	1510	209.0 (45.8)
2d	86	219–220	1592	206.9 (46.5)
2e	85	203–204	1535	209.5 (45.8)
2f	81	250–251	1536	209.6 (45.8)

3. Results and discussion

3.1. Synthesis and characterization of RhCl(COD)NHC

The bis(1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidene) (**1**), was synthesized using a method similar to that reported by Lappert and co-workers [20]. The reaction of bis(1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidene) (**1**), with the binuclear $[RhCl(COD)]_2$ complex proceeded smoothly in refluxing toluene to give the RhCl(COD)(1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidene) complexes (**2a–f**) as crystalline solids in 81–91% yields (Scheme 2, Table 1). Although compounds **2a–f** are available by the reactions of $[Rh(OMe)(COD)]_2$ with the appropriate 1,3-dialkyl-3,4,5,6-tetrahydropyrimidinium salts. The purification procedure

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



Entry	Catalyst	R_n	Time (h)	Yield (%)[a,b,c,d]
1	**2a**	*p*-Cl	4	93
2	**2b**	*p*-Cl	4	89
3	**2c**	*p*-Cl	8	72
4	**2d**	*p*-Cl	4	89
5	**2e**	*p*-Cl	8	74
6	**2f**	*p*-Cl	5	77
7	**2a**	2,4,6-$(CH_3)_3$	4	94
8	**2b**	2,4,6-$(CH_3)_3$	6	74
9	**2c**	2,4,6-$(CH_3)_3$	8	72
10	**2d**	2,4,6-$(CH_3)_3$	6	90
11	**2e**	2,4,6-$(CH_3)_3$	8	89
12	**2f**	2,4,6-$(CH_3)_3$	8	74
13	**2a**	3,4,5-$(OMe)_3$	4	87
14	**2b**	3,4,5-$(OMe)_3$	4	92
15	**2c**	3,4,5-$(OMe)_3$	7	85
16	**2d**	3,4,5-$(OMe)_3$	7	95
17	**2e**	3,4,5-$(OMe)_3$	5	81
18	**2f**	3,4,5-$(OMe)_3$	5	94
19	**2a**	2,5-$(OMe)_2$	6	91
20	**2b**	2,5-$(OMe)_2$	6	89
21	**2c**	2,5-$(OMe)_2$	6	87
22	**2d**	2,5-$(OMe)_2$	6	96
23	**2e**	2,5-$(OMe)_2$	6	93
24	**2f**	2,5-$(OMe)_2$	6	89
25	**2a**	*p*-$C(CH_3)_3$	4	92
26	**2b**	*p*-$C(CH_3)_3$	4	86
27	**2c**	*p*-$C(CH_3)_3$	7	76
28	**2d**	*p*-$C(CH_3)_3$	4	80
29	**2e**	*p*-$C(CH_3)_3$	10	87
30	**2f**	*p*-$C(CH_3)_3$	10	79

[a] *Reactions conditions*. Phenylboronic acid (9.8 mmol), aldehydes (4.9 mmol), rhodium-carbene (1 mmol%), KO*t*Bu (4.9 mmol), dimethoxyethane (15 mL).
[b] Isolated yield.
[c] Yields based on aldehydes.
[d] All reactions were monitored by GC.

is more complicated than this procedure with these N-substituted.

Complexes (**2a**–**f**), are very stable in the solid state and were characterized by analytical and spectroscopic techniques (Table 1). The rhodium complexes exhibit a characteristic $\upsilon_{(NCN)}$ band (Table 1) typically at 1510–1619 cm^{-1} [21]. ^{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 196.9–211.9 ppm and are similar to those found in other carbene complexes [18]. Coupling constants $J(^{103}Rh–^{13}C)$ for the new rhodium complexes (**2a**–**f**) 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 RhCl(COD)(1,3-dialkylbenzimidazolidin-2-ylidine) complexes [21].

3.2. Arylation of benzaldehyde derivatives

Although the addition of carbon nucleophiles to aldehydes is usually a facile process, limits are encountered when functionalized organometallic reagents are required. Rhodium complexes (**2a**–**f**) were found to be active catalysts for the addition of phenylboronic acid to aldehydes and proved to be thermally robust at 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-chlorobenzaldehyde, 2,4,6-trimethylbenzaldehyde, 3,4,5-trimethoxybenzaldehyde, 2,5-dimethoxybenzaldehyde, and 4-*tert*-butylbenzaldehyde react very cleanly with phenylboronic acid in goods yields (Table 2, entries 1, 7, 16, 19, 22, and 25). In general, bulky **2a** and methoxy substituted carbene complexes (**2b** and **2d**) afford superior yields than **2c**, **2e** and **2f**. The substitution pattern of the aldehyde has only a minor effect on the activity.

The obtained yields are similar to $[Rh(acac)(CO)_2]$/dppf and imidazoline based rhodium-carbene complexes systems, but the reactions time is shorter than $[Rh(acac)(CO)_2]$/dppf system [16,18].

While these studies were in progress, Buchmeiser and co-workers have addressed the synthesis and catalytic properties of 1,3-dimesityltetrahydropyrimidine-2-ylidene complexes of rhodium [14b]. Bolm and his co-workers [22] have applied an in situ prepared catalyst from a planar-chiral imidazolium salt and $[Rh(OAc)_2]_2$ and have achieved up to 38% ee.

3.3. Conclusion

From readily available starting materials, such as 1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidene, six rhodium-carbenes (**2a**–**f**) have been prepared and characterized. In addition, 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. Future investigations are aimed at the development of an asymmetric version of this process.

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