

Rhodium-benzimidazolidin-2-ylidene catalyzed addition of arylboronic acids to aldehydes

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Abstract

Six rhodium-carbene complexes (*2a-f*) have been prepared and the new compounds characterized by C, H, N analyses, ¹H-n.m.r. and ¹³C-n.m.r. Phenylboronic acid reacts with aldehydes in the presence of a catalytic amount of rhodium(I)-carbene complex, RhCl(COD)(1,3-dialkylbenzimidazolidin-2-ylidene), (*2a-f*), to give the corresponding aryl secondary alcohols in good yields.

Introduction

The success of every organometallic catalyst system strongly depends on its availability and hence on convenient methods for its preparation. Recently, several efficient transition metal catalysts have been developed, derived from heterocyclic carbenes [1]. Homogeneous organometallic catalysis have long depended on phosphine ligands, PR₃ [2]. Only recently have *N*-heterocyclic carbenes (NHCs) offered the promise of an alternative ligand environment for organometallic catalysis [3]. These new ligands proved to be competitive with classical phosphines in many respects [4]. For example, the synthesis of the carbene precursors usually involves straightforward nitrogen quaternization to form *N, N'*-disubstituted imidazolium salts. Methodologies for the metallation of such imidazolium salt precursors is therefore of substantial current interest and a number of methods have been established. In their pioneering work, Lappert and coworkers used electron-rich alkenes (entetramines) as the ligands [5]. The C=C double bond in these alkenes could be activated by various metal salts to give the corresponding metallated carbenes. By far the most common route to prepare a metal-carbene bond, however, is the free carbene route, involving the abstraction of the acidic azolium proton with BuLi, ^tBuOK or NaH and trapping of the free carbene, after isolation or *in situ*, [6] with a metal precursor [7].

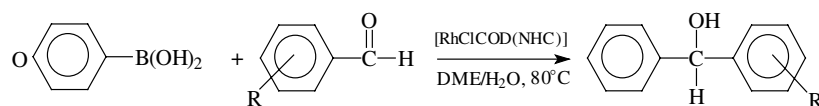
The recent transition metal *N*-heterocyclic carbene complexes have been employed as catalysts for Heck and Suzuki coupling reactions [8], olefin metathesis [9], hydroformylation, hydrogenation and hydrosilylation [10, 11], and the copolymerization of ethane and CO [12].

Our contribution to this field started with syntheses of imidazolidin-2-ylidenes complexes of rhodium(I) and ruthenium(II) which are capable of catalyzing the cyclopropanation of styrene with ethyl diazoacetate [13], intramolecular cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol onto 2,3-dimethylfuran, and addition of phenylboronic acid to aldehydes in good yields [14, 15]. A highly effective, easy to handle and environmentally benign process for palladium-mediated Suzuki cross-coupling was developed [16]. 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 and to evaluate their ability to chelate the ruthenium atom, stabilize the complex, or create catalytic activity [17].

Rhodium-carbene complexes have been extensively studied. However, there are few reports on the catalytic activity of rhodium-carbene complexes in rhodium-mediated processes [18, 19]. 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 [20]. 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 the rhodium salt, 1,3-dialkylimidazolium chloride and base [21].

Based on these findings and our continuing interest in developing more efficient and stable catalysts, we wished

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Scheme 1.

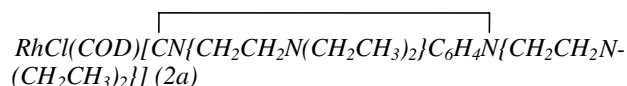
to examine whether we could influence the catalytic activity of rhodium-benzimidazolidin-2-ylidene complexes for the addition of phenylboronic acid to aldehydes (Scheme 1). We now report: (i) the straightforward preparation of new RhCl(COD)(1,3-dialkylbenzimidazolidin-2-ylidene) complexes and (ii) their efficient catalysis for the addition of phenylboronic acid to aldehydes.

Experimental

All manipulations were prepared by standard Schlenk techniques under an inert atmosphere of nitrogen with previously dried solvents. Solvent and reagents were obtained from Aldrich, Merck and Across Chemicals. The complex [RhCl(COD)]₂ [22], 1,3-dialkylbenzimidazolinium salts and 1,3-dialkylbenzimidazolidinylidene (*1*) were prepared according to known methods [23]. I.r. spectra were recorded as KBr pellets in the 400–4000 cm⁻¹ range on a ATI UNICAM 2000 spectrometer. ¹H-n.m.r. (400 MHz) and ¹³C-n.m.r. (100 MHz) were recorded on a Bruker AM 400 WB FT spectrometer with chemical shifts referenced to residual solvent CDCl₃. Microanalyses were performed by the TÜBITAK Analyses Center.

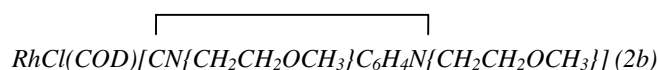
General procedure for the preparation of the rhodium-carbene complexes

A solution of bis[1,3-dialkylbenzimidazolidin-2-ylidene] (*1*) (0.5 mmol) and [RhCl(COD)]₂ (0.5 mmol) in PhMe (15 cm³) were heated under reflux for 2 h. Upon cooling to room temperature, yellow crystals (*2a-f*) were obtained. The crystals were filtered, washed with Et₂O (3 × 15 cm³) and dried under vacuum.

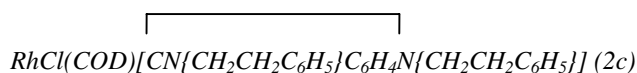


Yield: 0.25 g, 90%, m.p. 140–141 °C. I.r., ν_{CN} : 1474 cm⁻¹. (Found: C, 57.6; H, 7.6; N, 9.7. C₂₇H₄₄N₄RhCl calcd.: C, 57.6; H, 7.9; N, 9.9%). ¹H-n.m.r. (CDCl₃): δ 1.13 (t, $J = 7.2$ Hz, 12H, CH₂CH₃); 2.70 (quar., $J = 3.6$ Hz, 8H, CH₂CH₃); 2.79 and 3.18 (t, $J = 6.8$ Hz and $J = 7.2$ Hz, 4H, NCH₂CH₂N); 3.29 and 4.55 (t, $J = 7.6$ Hz, 4H, NCH₂CH₂N); 7.15 and 7.27 (m, 4H, C₆H₄); 5.08 and 5.13 (d, $J = 6.4$ Hz, 4H CH₂CO₂); 1.94 (quar., $J = 8.8$ Hz, 4H, CH₂CO₂); 2.38 (m, 4H, CH₂CO₂). ¹³C-n.m.r. (CDCl₃): δ 196.5 (d, $J = 50.3$ Hz, C_{carbene}); 12.6 (CH₂CH₃); 48.4 (CH₂CH₃); 47.6–51.9

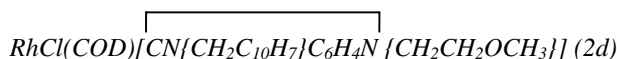
(CH₂CH₂); 110.1, 122.5, 134.9 (C₆H₄); 69.0 and 100.4 (d, $J = 6.9$ Hz and $J = 14.5$ Hz, CH₂CO₂); 29.0 and 33.2 (CH₂CO₂).



Yield: 0.21 g, 86%, m.p. 134–136 °C. I.r., ν_{CN} : 1476 cm⁻¹. (Found: C, 52.3; H, 6.6; N, 5.7. C₂₁H₃₀N₂O₂RhCl calcd.: C, 52.5; H, 6.3; N, 5.8%). ¹H-n.m.r. (CDCl₃): δ 3.37 (s, 6H, OCH₃); 4.02 (m 4H, NCH₂CH₂O); 4.84 (m, 4H, NCH₂CH₂O); 7.19 and 7.45 (m, 4H, C₆H₄); 5.17 (t, $J = 5.6$ Hz, 4H CH₂CO₂); 2.00 and 2.43 (m, 8H, CH₂CO₂). ¹³C-n.m.r. (CDCl₃): δ 196.9 (d, $J = 51.3$ Hz, C_{carbene}); 71.8 (OCH₃); 48.7 (NCH₂CH₂O); 59.3 (NCH₂CH₂O); 110.9, 122.5, 135.6 (C₆H₄); 69.3 and 100.5 (d, $J = 6.1$ Hz and $J = 14.5$ Hz, CH₂CO₂); 29.0 and 33.1 (CH₂CO₂).

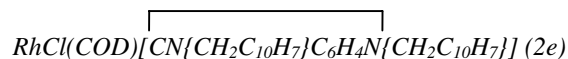


Yield: 0.26 g, 91%, m.p. 192–194 °C. I.r., ν_{CN} : 1483 cm⁻¹. (Found: C, 64.6; H, 5.9; N, 4.6. C₃₁H₃₄N₂RhCl calcd.: C, 64.9; H, 5.9; N, 4.9%). ¹H-n.m.r. (CDCl₃): δ 3.16 and 3.53 (t, $J = 5.6$ Hz and $J = 6.0$ Hz, 4H, NCH₂CH₂); 3.28 (m, 2H NCH₂CH₂); 4.76 (t, $J = 5.6$ Hz, 2H, NCH₂CH₂); 7.12–7.18 (m, 4H, C₆H₄); 7.21 (t, $J = 4.0$ Hz, 2H, *p*-CH₂CH₂-C₆H₅); 7.31 (t, $J = 7.2$ Hz, 4H, *m*-CH₂CH₂-C₆H₅); 7.39 (d, $J = 7.2$ Hz, 4H, *o*-CH₂CH₂-C₆H₅); 5.19 (m, 4H, CH₂CO₂); 1.96 and 2.37 (m, 8H, CH₂CO₂). ¹³C-n.m.r. (CDCl₃): δ 196.6 (d, $J = 50.3$ Hz, C_{carbene}); 36.4 (NCH₂CH₂); 50.6 (NCH₂CH₂); 110.1, 122.5, 134.8 (C₆H₄); 69.0 and 100.5 (d, $J = 6.9$ Hz and $J = 14.5$ Hz, CH₂CO₂); 29.1 and 33.2 (CH₂CO₂).

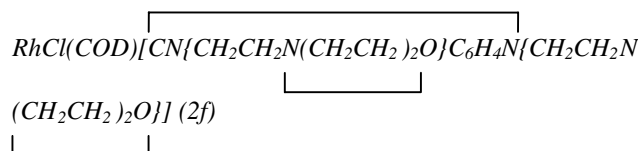


Yield: 0.22 g, 79%, m.p. 187–188 °C. I.r., ν_{CN} : 1479 cm⁻¹. (Found: C, 61.6; H, 5.9; N, 4.6. C₂₉H₃₂N₂ORhCl calcd.: C, 61.9; H, 5.7; N, 5.0%). ¹H-n.m.r. (CDCl₃): δ 3.44 (s, 3H, OCH₃); 3.26 (m 2H, NCH₂CH₂O); 4.10 (m, 2H, NCH₂CH₂O); 5.10 (s, 2H, CH₂C₁₀H₇); 6.90–8.37 (m, 14H, C₆H₄ and CH₂C₁₀H₇); 5.05 and 5.20 (m, 2H, CH₂CO₂); 6.21 (d, 2H, $J = 6.1$ Hz, CH₂CO₂); 1.62–2.39 (m, 8H, CH₂CO₂). ¹³C-n.m.r. (CDCl₃): δ 198.1 (d, $J = 50.3$ Hz, C_{carbene}); 71.9 (OCH₃); 48.9 (NCH₂CH₂O); 59.4 (NCH₂CH₂O); 110.9, 122.7, 135.9 (C₆H₄); 50.3 (CH₂C₁₀H₇); 123.8, 125.6, 126.4, 127.1, 128.3, 129.2,

130.7, 131.9, 133.9, 135.2 ($\text{CH}_2\text{C}_{10}\text{H}_7$); 69.3 and 69.5 (d, $J = 13.7$ and 14.5 Hz, CH_{COD}); 100.3 and 100.9 (d, $J = 14.5$ Hz and $J = 6.9$ Hz, CH_{COD}); 28.8 and 32.6 (CH_2COD).



Yield: 0.24 g, 75%, m.p. 278–279 °C. I.r., ν_{CN} : 1481 cm^{-1} . (Found: C, 68.6; H, 5.6; N, 4.5. $\text{C}_{37}\text{H}_{34}\text{N}_2\text{RhCl}$ calcd.: C, 68.9; H, 5.3; N, 4.3%). ^1H -n.m.r. (CDCl_3): δ 4.99 (s, 2H, $\text{CH}_2\text{C}_{10}\text{H}_7$); 6.90–8.35 (m, 14H, C_6H_4 and $\text{CH}_2\text{C}_{10}\text{H}_7$); 6.23 (d, 4H, $J = 16$ Hz, CH_{COD}); 1.44–2.29 (m, 8H, CH_2COD). ^{13}C -n.m.r. (CDCl_3): δ 199.7 (d, $J = 51.1$ Hz, $\text{C}_{\text{carbene}}$); 50.4 ($\text{CH}_2\text{C}_{10}\text{H}_7$); 111.2, 123.0, 135.9 (C_6H_4); 123.8, 125.7, 126.5, 127.1, 128.5, 129.3, 130.9, 132.1, 133.6, 133.6 ($\text{CH}_2\text{C}_{10}\text{H}_7$); 69.5 and 100.7 (d, $J = 14.4$ Hz and $J = 6.8$ Hz, CH_{COD}); 28.5 and 32.8 (CH_2COD).



Yield: 0.25 g, 84%, m.p. 235–236 °C. I.r., ν_{CN} : 1477 cm^{-1} . (Found: C, 54.6; H, 6.9; N, 9.1. $\text{C}_{27}\text{H}_{40}\text{N}_4\text{O}_2\text{RhCl}$ calcd.: C, 54.9; H, 6.8; N, 9.5%). ^1H -n.m.r. (CDCl_3): δ 2.68 (m 8H, $\text{NCH}_2\text{CH}_2\text{O}$); 3.75 (t, $J = 13.7$ Hz, 8H, $\text{NCH}_2\text{CH}_2\text{O}$); 3.35; 4.78; 2.89 and 3.13 (m, 8H, $\text{NCH}_2\text{CH}_2\text{N}$); 7.21

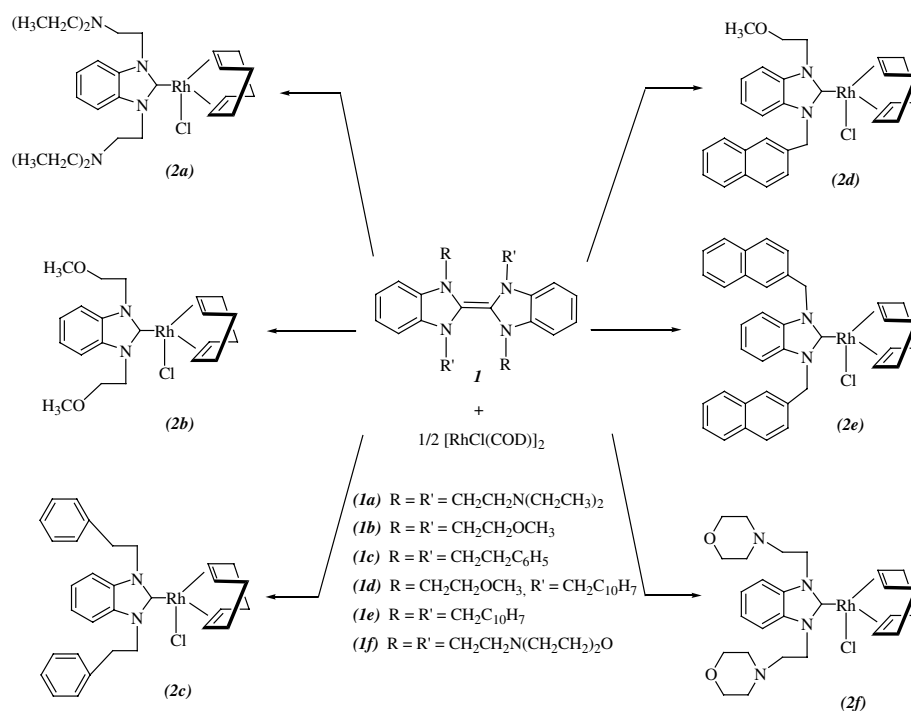
and 7.36 (m, 4H, C_6H_4); 5.12 (m, 4H, CH_{COD}); 2.01 (quar., $J = 8.4$ Hz, 4H, CH_2COD); 2.43 (m, 4H, CH_2COD). ^{13}C -n.m.r. (CDCl_3): δ 197.3 (d, $J = 50.3$ Hz, $\text{C}_{\text{carbene}}$); 57.6 ($\text{NCH}_2\text{CH}_2\text{O}$); 67.2 ($\text{NCH}_2\text{CH}_2\text{O}$); 46.3 and 54.2 ($\text{NCH}_2\text{CH}_2\text{N}$); 110.3, 122.6, 135.0 (C_6H_4); 69.0 and 100.6 (d, $J = 14.5$ Hz and $J = 6.9$ Hz, CH_{COD}); 29.1 and 33.2 (CH_2COD).

General procedure for Rhodium–carbene catalyzed addition of phenylboronic acid to aldehydes.

Phenylboronic acid (1.20 g, 9.8 mmol), $\text{KOBu-}t$ (4.9 mmol), the substituted aldehyde (4.9 mmol), rhodium carbene catalyst (1 mol%) and dimethoxyethane (15 cm^3) were introduced in to Schlenk tube and then H_2O (5 cm^3) was added. The resulting mixture was heated for 1.0–2.0 h at 80 °C, cooled to ambient temperature, extracted by ethyl acetate (30 cm^3). After drying over MgSO_4 the organic phase was evaporated and the residue was purified by flash chromatography. The isolated yield (purity of yield and yields based on aldehydes) was checked by n.m.r. All reactions were monitored by t.l.c.

Results and discussion

The tetraaminoethene, (*1*), was synthesised using a method similar to that reported by Lappert and Co-workers [23c] The reaction of tetraaminoethene (*1*) with the binuclear $[\text{RhCl}(\text{COD})]_2$ complex proceeded smoothly in refluxing toluene to give the $\text{RhCl}(\text{COD})(1,3\text{-dialkylbenzimidazolinyli-})$ complexes (*2a-f*) as crystalline solids in 75–91% yields (Scheme 2).



Scheme 2. Synthesis of rhodium–carbene complexes.

Complexes (*2a–f*), which are very stable in the solid state, have been characterized by analytical and spectroscopic techniques. Rhodium complexes exhibit a characteristic $\nu_{(\text{NCN})}$ band typically at 1474–1483 cm^{-1} [14, 24]. ^{13}C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that C_{carb} is substantially deshielded. Values of $\delta(^{13}\text{C}_{\text{carb}})$ are in the 196.5–199.7 ppm range and are similar to those found for other carbene complexes. Coupling constants $J(^{103}\text{Rh}-^{13}\text{C})$ for the new rhodium complexes (*2a–f*) 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 other $\text{RhCl}(\text{COD})(1,3\text{-dialkylbenzimidazolidin-2-ylidene})$ complexes [14, 25]. Although the addition of carbon nucleophiles to aldehydes is usually a facile process, limits are encountered that the functionalized organometallic reagents require. 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, quite rapidly even with a low catalyst loading. The results were summarized in

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

Entry	Cat.	R	Time (h)	Yield (%) ^{a,b,c}
1	2a	OCH ₃	1.5	89
2	2b	OCH ₃	1.0	92
3	2c	OCH ₃	1.5	87
4	2d	OCH ₃	1.5	90
5	2e	OCH ₃	1.5	88
6	2f	OCH ₃	2.0	90
7	2a	2,4,6-(OCH ₃) ₃	1.5	89
8	2b	2,4,6-(OCH ₃) ₃	1.0	91
9	2c	2,4,6-(OCH ₃) ₃	2.0	83
10	2d	2,4,6-(OCH ₃) ₃	2.0	86
11	2e	2,4,6-(OCH ₃) ₃	2.0	85
12	2f	2,4,6-(OCH ₃) ₃	2.0	79
13	2a	3,4,5-(OCH ₃) ₃	2.0	92
14	2b	3,4,5-(OCH ₃) ₃	2.0	97
15	2c	3,4,5-(OCH ₃) ₃	1.0	84
16	2d	3,4,5-(OCH ₃) ₃	1.5	96
17	2e	3,4,5-(OCH ₃) ₃	1.5	94
18	2f	3,4,5-(OCH ₃) ₃	1.0	88
19	2a	2,4,6-(CH ₃) ₃	1.5	92
20	2b	2,4,6-(CH ₃) ₃	1.0	97
21	2c	2,4,6-(CH ₃) ₃	2.0	91
22	2d	2,4,6-(CH ₃) ₃	2.0	85
23	2e	2,4,6-(CH ₃) ₃	1.0	91
24	2f	2,4,6-(CH ₃) ₃	1.0	90
25	2a	Cl	1.0	88
26	2b	Cl	1.0	94
27	2c	Cl	1.0	92
28	2d	Cl	1.0	91
29	2e	Cl	1.0	89
30	2f	Cl	1.0	88

^aIsolated yield (purity of yield checked by n.m.r.).

^bYields based on aldehydes.

^cAll reactions were monitored by t.l.c.

Table 1. Under those conditions, 4-methoxybenzaldehyde, 2,4,6-trimethylbenzaldehyde, 3,4,5-trimethoxybenzaldehyde and 4-chlorobenzaldehyde react very cleanly with phenylboronic acid to give good product yields (Table 1, entry 2, 8, 14, 20 and 26).

Conclusion

From readily available starting materials, such as 1,3-dialkylbenzimidazolinyldene, six rhodium–carbene (*2a–f*) 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. Future investigations are aiming at the development of an asymmetric version of this process.

Acknowledgements

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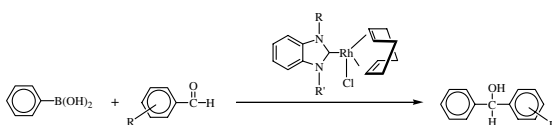
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Graphical abstracts



Rhodium-benzimidazolidin-2-ylidene catalyzed addition of arylboronic acids to aldehydes

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