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N-heterocyclic carbene complexes of Rh(I) and electronic effects on catalysts for 1,2-addition of phenylboronic acid to aldehydes

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1,3-Diarylsubstituted imidazolinium salts, (NHC-H)Cl, 3, containing hydrogen or alkyl groups at the 4,5-positions of the imidazolidine ring, served as precursors to rhodium(I) complexes [RhCl(NHC)COD], 4, which were converted into *cis*-[RhCl(NHC)$(CO)_2$] complexes, 5. All compounds prepared were characterized by elemental analyses, ^{1}H NMR and ^{13}C NMR. The relative σ-donor/π-acceptor strength of the NHC ligands was determined by means of IR spectroscopy of 5. The ability of NHCs in 4 to enchance activity was explored in the 1,2-addition of phenylboronic acid to aldehydes. A good correlation was observed between catalytic activity and the electron-donating power of the NHC ligands. Copyright © 2010 John Wiley & Sons, Ltd.

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Keywords: arylation; diarylmethanol; rhodium; electronic effects; imidazol-2-ylidene; NHC

Introduction

During the last 15 years, the synthesis and applications of *N*-heterocyclic carbene (NHC) complexes have witnessed an explosive growth.[1–9] Among the NHC ligands studied, imidazol-2-ylidene and its saturated analog imidazolin-2-ylidene are the most common and they are now known as normal NHCs which are good σ-donors, but weak π-acceptors.[10] As a result, NHCs are often compared with phosphines for catalytic reactions. It has been established that the complexes such as **I** offer the distinctive advantage of greater stability over the classical M/phosphine systems as the latter suffer from sensitivity to air, moisture and heating.[1] Furthermore, the structure of the NHC ligands can be altered by a modular approach. The preparation procedures developed allow multiple variations in the nature of the substituents on the nitrogen and carbon atoms on the ring.[11]

In a recent study on the complexes (**I**), we observed that the variation of the *p*-substituents (X) has a significant influence on the catalytic behavior of the Suzuki coupling of NHC–Pd complexes.[12] Only a few references referring to 4,5-substituted imidazol(in)-2-ylidene ligands can be found in the literature.[13] On the other hand, the rhodium-catalyzed 1,2-addition of aryl boronic acids has also enjoyed significant development: *in situ* formed and preformed NHC complexes of rhodium have been successfully applied to 1,2-arylations of aldehydes.[14,15] However, some questions concerning the influence of steric and electronic properties of the NHC ligands remain unanswered and deserve a detailed examination. Therefore, the main aim of this paper was to modify the *p*-substituent of the aryl moiety (ring A) and 4,5-position of of the imidazolidine (ring B) to quantify the electronic influence of X, R and R′ substituents on the catalytic activities of **II** (Scheme 1).

Results and Discussion

Synthesis and Characterization of Ligand Precursors and Complexes

The structures of NHC complexes can be modified in several ways to tune their electronic properties, which are important for homogeneous catalysis.[1] The desired NHC precursors (**3**) and Rh(I) complexes (**4**) derived from them were synthesized according to Scheme 2. Apart from these complexes, unsymmetrical aryl containing NHC complex (**4i**) was also included for comparison.

A combination of commercially available anilines and 1,2-diones with varying steric and electronic substituents was used to obtain diimines (**1**), which were reduced to diamines (**2**) by means of $NaBH_3CN$ and than the diamines were cyclized into imidazolinium chlorides (**3**) via $CH(OEt)_3$ in the presence of chloride. These salts were deprotonated by $[Rh(\mu\text{-OMe})COD]_2$ to afford the (NHC)-Rh(I) complexes, **4** (Scheme 2). The resulting compounds, which contain hydrogen, alkyl or a combination of these groups on the C_4–C_5 positions of the imidazolidine ring and aryl groups on the nitrogen atoms, were characterized by ^{1}H NMR and ^{13}C NMR. The ^{1}H NMR spectra of these salts exhibit characteristic NHC-H resonance around $\delta = 9.72$–9.82 ppm. The formation of the salts is also supported by a resonance around $\delta = 158.0$–159.9 ppm in the ^{13}C NMR spectrum for the NHCN carbon atom.

The structurally and sterically similar 1,3-bis(2,6-dimethylphenyl)imidazolinium salts containing H, CH_3, Br and Cl groups are known in the literature.[12] Rh–NHC complex (**4**) was obtained

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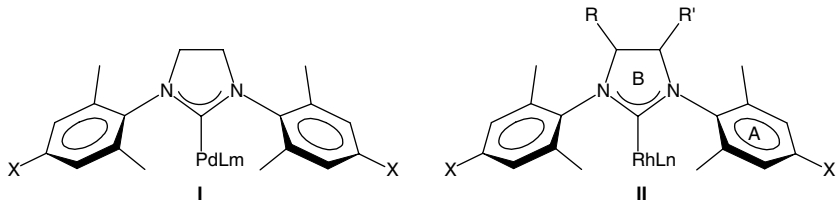
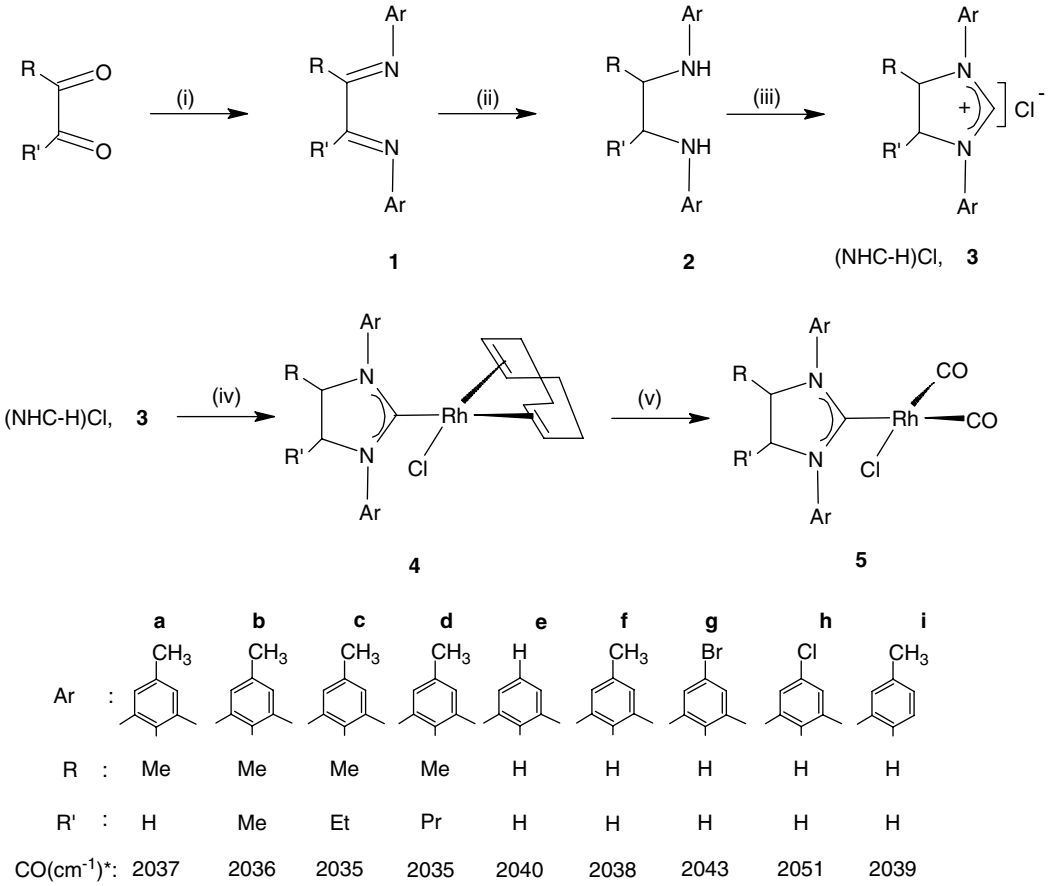


Scheme 1. Structural ring represantation of NHCs and N-substitents.



Scheme 2. Synthesis of imidazolinium salts, **3**, rhodium complexes, **4** and **5**, and average carbonyl stretching wavenumbers (cm^{-1}) of **5** in CH_2Cl_2. The asterisk refers to the average carbonyl stretching frequencies of **5**. Reagent and conditions: (i) Ar–NH_2, EtOH, RT; (ii) $NaCNBH_3$, MeOH, RT, 24 h, after 65 °C, 8 h; (iii) NH_4Cl, $HC(OEt)_3$, 130 °C, 4 h; (iv) $[(Rh(OMe)(COD)]_2$, $PhCH_3$, 110 °C, 2 h; (v) CO, CH_2Cl_2, 0.5 h.

through reaction of imidazolinium salt (**3**) using the basic character of $[Rh(\mu\text{-OMe})(COD)]_2$. Rhodium complexes are stable crystalline substances, the structures of which have been elucidated by NMR spectroscopy. ^{13}C chemical shifts, which provide a useful diagnostic tool for Rh–carbene complexes, show that C_{carb} is substantially deshielded. Values of $\delta(^{13}C_{carb})$ are in the range $\delta = 209.6–215.2$ ppm.

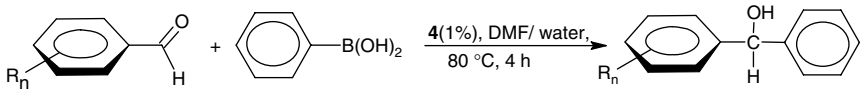
Direct comparison of the electronic properties of NHCs could be done measuring the carbonyl stretching frequencies of NHC-containing carbonyl complexes such as $[(NHC)\text{-}Ni(CO)_3]$, $[RhX(NHC)(CO)_2]$ or $[IrX(NHC)(CO)_2]$: more basic ligands induce lower stretching frequencies.[16–21] Thus, the carbonyl complexes of type **5** have been synthesized by replacing the COD ligand with excess CO.

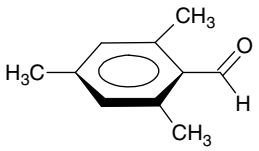
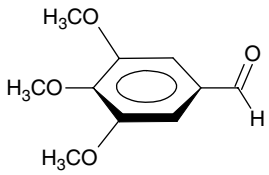
The IR spectra of the complexes allowed us to evaluate simultaneously subtle electronic influence of H, Me, Br and Cl as well as R and R′ groups without possible complications due to steric effects. The C–O stretching frequencies in $[RhCl(NHC)(CO)_2]$ complexes which derived from **4** are sensitive to the substituent at the *p*-position of the phenyl ring of the 1,3-disubstituted imidazolidine ring if we ignore the contribution of the $C_4–C_5$ substitution. The $\nu_{(CO)av}$ data, given in Scheme 2, indicate that the basicity decreases in the following order: **d** = **c** > **b** > **a** > **i** > **f** > **e** > **g** > **h**. However, the backbone alkyl substituents on the imidazolin-2-ylidene ring also significantly increase the donor ability. This observation is consistent with the literaturedata.[20g] The ^{13}C NMR spectra of *cis*-$[RhCl(CO)_2NHC]$ complexes (**5**) gave a carbenic signal at 205.7–206.8 ppm as a doublet. Coupling constants $J(^{13}C–^{103}Rh)$ for **5** are in the range 41–42 Hz.

Catalytic Experiments

Catalyst testing was conducted in order to access the effects of X, R, R′ substituents on the NHC ligands to catalyze arylation of

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



Entry	4	Aldehyde	Yield (%)[a]
1	**a**		89
2	**b**		90
3	**c**		91
4	**d**		90
5	**e**		78
6	**f**		90
7	**g**		66
8	**h**		65
9	**i**		43
10	**a**		84
11	**b**		90
12	**c**		91
13	**d**		87
14	**e**		82
15	**f**		89
16	**g**		63
17	**h**		60
18	**i**		45
19	**a**		83
20	**b**		94
21	**c**		94
22	**d**		93
23	**e**		80
24	**f**		93
25	**g**		67
26	**h**		58
27	**i**		37
28	**a**		93
29	**b**		92
30	**c**		90
31	**d**		89
32	**e**		79
33	**f**		88
34	**g**		64
35	**h**		61
36	**i**		33

[a] Yields were determined by gas chromatography for an average of three runs.

aldehydes using $PhB(OH)_2$ as source of aryl and the products were analyzed by GC. For the sake of comparison, the previously used conditons were chosen: the addition of phenylboronic acid to aromatic aldehydes with 1 mol% of catalyst **4** in the presence of $KOBu^t$–$PhB(OH)_2$ (1 : 2) in DMF–H_2O (3 : 1) was screened at 80 °C. The data in Table 1 reveal that complexes **4a–4d** and **4f** are efficient and the relative activity sequence after 4 h is **b** ≈ **c** ≈ **d** ≈ **a** ≈ **f** > **e** > **g** > **h** > **i**. The activities of the different catalysts (Table 1) range from 33% for catalyst **4i** up to 94% for catalysts **4a–4d**. The addition of phenylboronic acid to aldehydes proceeded in high yields and quite rapidly, even with a low catalyst loading. Under those conditions, 4-methoxybenzaldehyde, 2,4,6-trimethylbenzaldehyde, 3,4,5-trimethoxybenzaldehyde and 4-chlorobenzaldehyde reacted cleanly to good yields (Table 1, entries 3, 12, 20, 21 and 29). We could show that electron-rich and bulky NHC ligands lead to a higher activity with yields up to 94%.

Compound **4b** appears to be the most active catalyst; but **4a**, bearing one Me at the 4-position, is similar to SIMes (**4f**). This sequence can be explained on the basis of electron-donating groups present both at the *p*-position of the aryl and the 4,5-positions of the imidazolidine rings. It is clear that the alkyls as electron releasing groups increase the rate of arylation. The length of the alkyl chain at the 4,5-positions seems not to be influential. The 2,4-dimethyl derivative **4i**, an isomer of **4e**, exhibited the lowest activity of the nine complexes tested. A similar trend was observed in the NHC-Pd catalyzed Suzuki–Miyaura coupling.[12]

This observation again stresses the importance of steric factors as well as electronic parameters.

With the exception of **4i** and **4f**, comparison of both the catalytic activity of [RhCl(NHC)COD] and IR data on [RhCl(NHC)$(CO)_2$] clearly demostrated that there is a good correlation between electron donation power and catalytic effciency.

Conclusion

The electronic effect of substituents on the 1,2-addition reaction rate of phenylboronic acid to aldehydes was studied by varying the substituents in both rings (i.e. A and B of NHC, in structure II). The general trend observed in most cases was that electron releasing groups increased the efficiency while electron–withdrawing groups retarded the reaction rate. The X group on the phenyl ring had a significant influence wheras the R and R′ groups at the 4,5-positions of the imidazolidine ring appeared to play a less important role in the complex's catalytic activity. In particular, **4b** and **4c** bearing methyl, ethyl at the C_4–C_5 positions of the imidazolidine ring showed better catalytic activity. These studies allowed us to compare the *p*-position of the phenyl ring of the 1,3-disubstituted imidazolidin ring and the C_4–C_5 positions of the imidazolidine ring.

Based on CO IR streching frequencies, the following complexes can be ranked from most electron-rich to least: **d** = **c** > **b** > **a** > **i** > **f** > **e** > **g** > **h**.

Experimental

All reactions for the preparation of salts were carried out under Ar in flame-dried glassware using standard Schlenk-type flasks. Anhydrous solvents were either distilled from appropriate drying agents or purchased from Merck and degassed prior to use by purging with dry argon and standing over molecular sieves. NMR spectra were recorded at 297 K on a Varian Mercury AS 400 at 400 MHz (^{1}H), 100.56 MHz (^{13}C). Elemental analyses were carried out using the analytical service of Tubıtak with a Carlo Erba Strumentazione Model 1106 apparatus. Rhodium comlexes derived from **3b** were recently published.[16] The other compounds were prepared according to the literature procedures.[12,16]

1a. To a solution of 2,4,6-trimethylaniline (2.0 g, 14.8 mmol) in 100 ml ethanol was added at 25 °C a mixture of a 35% aqueous solution of methylglyoxal (0.54 g, 7.4 mmol). The resulting yellow precipiate was collected by filtration and dried in vacuum. Yield: 2.08 g, 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1 H, N=CH) 6.92 (s, 2 H, Ar–H), 6.90 (s, 2 H, Ar–H), 2.30, 2.22, 2.17, 2.03, 2.01 (s, 21 H, N=CCH_3, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5 (N=C) 145.0, 128.8, 128.7, 128.5, 128.4, 126.6, 124.5 (Ar–C), 20.7, 20.6, 18.1, 17.6 (Ar–CH_3), 14.9 (N=CCH_3). Anal. calcd for $C_{21}H_{26}N_2$ (M = 306.4): C, 82.31; H, 8.55; N, 9.14. Found: C, 82.32; H, 8.52; N, 9.18%.

The compound **1c** was prepared in the same way as **1a** from 2,4,6-trimethylaniline (2.0 g, 14.8 mmol) and 2,3-pentandione (0.82 g, 7.4 mmol) to give yellow crystals of **1c**. Yield: 2.18 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (s, 2 H, Ar–H), 6.89 (s, 2 H, Ar–H), 2.55 (q, 2 H, J = 3.3 Hz, N=CC$H_2$$CH_3$), 2.29 (s, 3 H, N=C$CH_3$), 2.03, 2.02, 2.00, 1.94 (s, 18 H, Ar–CH_3), 1.06 (t, 3 H, J = 3.3 Hz, N=C$CH_2$$CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 167.6 (N=C) 146.0, 145.6, 132.4, 132.3, 128.7, 128.6, 124.6, 124.5 (Ar–C), 22.2 (NCH_3), 20.7 (N=C$CH_2$$CH_3$), 17.9, 17.8, 17.7, 16.7 (Ar–CH_3), 11.4 (N=C$CH_2$$CH_3$). Anal. calcd for $C_{23}H_{30}N_2$ (M = 334.5): C, 82.59; H, 9.04; N, 8.37. Found: C, 82.62; H, 9.01; N, 8.38%.

The compound **1d** was prepared in the same way as **1a** from 2,4,6-trimethylaniline (2.0 g, 14.8 mmol) and 2,3-hexanedione (0.84g, 7.4 mmol) to give yellow crystals of **1d**. Yield: 2.34 g, 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (s, 2 H, Ar–H), 6.88 (s, 2 H, Ar–H), 2.51 (t, 2 H, J = 4.0 Hz, N=CC$H_2$$CH_2CH_3$), 2.30 (s, 3 H, N=C$CH_3$), 2.02 (s, 18 H, Ar–$CH_3$), 1.53 (m, 2 H, N=C$CH_2$$CH_2CH_3$), 0.84 (t, 3 H J = 3.9 Hz, N=C$CH_2CH_2$$CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 167.8 (N=C) 145.9, 145.3, 132.3, 132.2, 128.9, 128.5, 124.6, 124.5 (Ar–C), 31.1 (N=C$CH_2CH_2CH_3$), 20.7 (N=CCH_3), 20.6 (N=C$CH_2CH_2CH_3$), 17.9, 17.8, 17.4, 16.3 (Ar–CH_3), 14.5 (N=C$CH_2CH_2CH_3$). Anal. calcd for $C_{24}H_{32}N_2$ (M = 334.5): C, 82.71; H, 9.25; N, 8.04. Found: C, 82.72; H, 9.31; N, 8.08%.

General Procedure for 2

A suspension of **1** (12.5 mmol) in MeOH (50 ml) was treated at room temparature under argon with $NaCNBH_3$ (3.92 g, 62.5 mmol) in portions of 1 g over a period of 20 min. To the mixture was added bromo cresole green until a color change from green to yellow occurred, then 0.1 M HCl was added to the solution which was stirred for 24 h and heated subsequently for 8 h under reflux. It was cooled to room temparature and 0.1 M (15 ml) KOH solution, 100 ml H_2O and CH_2Cl_2 were added. The water phase was washed with CH_2Cl_2 for a few more times. After the washing steps all of the CH_2Cl_2 phases were combined and dried with $MgSO_4$. The solvent was concentrated and then ethanol was added. The precipitate was filtered and washed with ethanol. Drying under vacuum provided NMR spectroscopically pure off-white crystals of **2**.

2a. Yield: 3.93 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (br, 2 H, Ar–H), 6.74 (br, 2 H, Ar–H), 3.29 [m, 1 H, N(CH_3)$CH$$CH_2$N], 3.20 [m, 2 H, N($CH_3$)CH$CH_2$N], 2.23, 2.17, 2.14, 1.94 (s, 18 H, Ar–CH_3), 1.17 [d, 3 H J = 3.0 Hz, N(CH_3)CHCH_2N]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 167.3 (N=C) 146.1, 140.6, 131.9, 131.3, 128.4, 128.0, 125.1, 124.7 (Ar–C), 53.0, 51.9 [N(CH_3)$CH$$CH_2$N], 17.9, 17.8, 17.7, 16.7, 15.9 [Ar–CH_3, N(CH_3)CHCH_2N]. Anal. calcd for $C_{21}H_{30}N_2$ (M = 310.5): C, 81.24; H, 9.74; N, 9.02. Found: C, 81.22; H, 9.80; N, 9.16%.

2c. Yield: 3.94 g, 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (br, 2 H, Ar–H), 3.29–3.14 [m, 2 H, N(CH_3)$CH$$CH$($CH_2CH_3$)N], 2.23, 2.17, 2.14, 1.94 (s, 18 H, Ar–CH_3), 1.83 [m, 2 H, N(CH_3)CHCH(CH_2CH_3)N], 1.18 [d, 3 H, J = 3.3 Hz, N(CH_3)CHCH(CH_2CH_3)N], 1.05 [t, 3 H, J = 3.4 Hz, N(CH_3)CHCH($CH_2$$CH_3$)N]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 167.6 (N=C) 146.0, 145.6, 132.4, 132.3, 128.7, 128.6, 124.6, 124.5 (Ar–C), 52.9, 51.7 [N(CH_3)CHCH(CH_2CH_3)N], 22.2, 20.7, 17.9, 17.8, 17.7, 16.7, 11.4 [Ar–CH_3, N(CH_3)CHCH(CH_2CH_3)N]. Anal. calcd for $C_{23}H_{34}N_2$ (M = 338.5): C, 81.60; H, 10.12; N, 8.28. Found: C, 81.62; H, 10.15; N, 8.36%.

2d. Yield: 3.74 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (br, 4 H, Ar–H), 3.28–3.24 [m, 2 H, HN(CH_3)$CH$$CH$($CH_2CH_2CH_3$)NH], 2.96 (br, 2 H, N$H$), 2.23, 2.18, 2.12 (s, 18 H, Ar–CH_3), 1.40–1.38 [m, 4 H, HN(CH_3)CHCH($CH_2$$CH_2CH_3$)NH], 1.14 [d, 3 H, J = 3.3 Hz, HNCH(CH_3)CH($CH_2CH_2CH_3$)NH], 1.05 [t, 3 H J = 3.4 Hz, HN(CH_3)CHCH($CH_2CH_2$$CH_3$)NH]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 129.6, 129.5, 129.4, 128.5 (Ar–C), 59.9, 54.1 [HN(CH_3)$CH$$CH$($CH_2CH_2CH_3$)NH), 33.7, 20.5, 20.4, 20.2, 19.1, 18.6, 18.6 [HN(CH_3)CHCH($CH_2$$CH_2CH_3$)NH, Ar–$CH_3$], 16.9 [HN($CH_3$)CHCH($CH_2CH_2CH_3$)NH], 14.4 [HN($CH_3$)CHCH($CH_2CH_2CH_3$)NH]. Anal. calcd for $C_{24}H_{36}N_2$ (M = 352.6): C, 81.76; H, 10.29; N, 7.95. Found: C, 81.72; H, 10.31; N, 8.03%.

General Procedure for 3

A mixture of **2** (10 mmol), triethyl orthoformate 10 ml and ammonium chloride (0.54 g, 10.2 mmol) was heated at 130 °C

in a distillation apparatus until ethanol distillation ceased. After cooling to RT, to the reaction mixture was added 50 ml diethyl ether. A colorless solid precipitated which was collected by filtration. Purification was achieved by repeated recrystallizations from ethanol–ether.

3a. Yield: 3.35 g, 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (s, 1 H, NCHN) 6.88 (s, 2 H, Ar–H), 6.86 (s, 2 H, Ar–H), 5.07–4.79 (m, 1 H, NC*H*CH_3CH_2N), 4.74 (m, 1 H, NCHCH_3C*H*$_2$N), 3.84 (m, 1 H, NCHCH_3*CH*$_2$N), 2.33, 2.29, 2.23, 2.22 (s, 18 H, Ar–CH_3), 1.41 (s, 3 H, NCH*H*$_3$$CH_2$N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6 (NCHN) 140.8, 139.9, 135.6, 134.8, 130.0, 129.9, 129.7, 128.5 (Ar–C), 60.1 (N*C*HCH_3CH_2N), 58.0 (NCHCH_3*CH*$_2$N), 20.9, 20.8, 18.8, 18.2 (Ar–*C*H$_3$), 17.8 (NCH*C*H$_3$). Anal. calcd for $C_{22}H_{29}N_2Cl$ (M = 356.9): C, 74.03; H, 8.19; N, 7.85. Found: C, 74.02; H, 8.22; N, 7.92%.

3c. Yield: 3.35 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1 H, NCHN), 6.90 (s, 2 H, Ar–H), 6.87 (s, 2 H, Ar–H), 5.12–5.07 [m, 2 H, N(CH_3)*CHCH*(CH_2CH_3)N], 3.84 [m, 2 H, N(CH_3)CHCH(CH_2CH_3)N], 2.30, 2.27, 2.24, 2.20 (s, 18 H, Ar–CH_3), 1.41 [s, 3 H, N(*CH*$_3$)CHCH(CH_2CH_3)N], 1.33 [s, 3 H, N(CH_3)CHCH(CH_2CH_3)N]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9 (NCHN) 141.0, 139.7, 136.5, 135.5, 131.1, 129.8, 128.6, 125.5 (Ar–C), 60.3, 58.0 [N(CH_3)CHCH(CH_2CH_3)N], 21.0, 20.7, 18.9, 18.7 (Ar–CH_3), 17.8, 17.5, 17.3 [N(*CH*$_3$)CHCH(*CH*$_2$$CH_3$)N]. Anal. calcd for $C_{24}H_{33}N_2Cl$ (M = 384.9): C, 74.87; H, 8.64; N, 7.28. Found: C, 74.92; H, 8.72; N, 7.20%.

3d. Yield: 3.35 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1 H, NCHN), 6.87 (s, 2 H, Ar–H), 6.83 (s, 2 H, Ar–H), 5.07–4.79 [m, 2 H, N(CH_3)*CHCH*($CH_2CH_2CH_3$)N], 3.00–2.55 [m, 4 H, N(CH_3)CHCH(*CH*$_2$*CH*$_2$$CH_3$)N], 2.30, 2.27, 2.24, 2.20 (s, 18 H, Ar–CH_3), 1.43 [s, 3 H, N(*CH*$_3$)CHCH($CH_2CH_2CH_3$)N], 1.30 [s, 3 H, N(CH_3)CHCH(CH_2CH_2*CH*$_3$)N]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0 (NCHN) 141.0, 138.4, 134.9, 133.9, 131.0, 129.0, 128.7, 128.5 (Ar–C), 58.7, 58.0 [N(CH_3)*CHCH*(CH_2CH_2*CH*$_3$)N], 22.7, 21.5, 20.9, 20.8, 18.8, 18.2, 17.4, 17.0 [Ar–*C*H$_3$, N(*CH*$_3$)CHCH(*CH*$_2$*CH*$_2$$CH_3$)N]. Anal. calcd for $C_{25}H_{35}N_2Cl$ (M = 399.0): C, 75.25; H, 8.84; N, 7.02. Found: C, 75.22; H, 8.88; N, 7.23%.

Synthesis of [RhCl(COD)(NHC)] Derivatives, 4

A mixture of imidazolinium salt (0.50 mmol) and [Rh(μ-OMe)(1,5-COD)]$_2$ (0.25 mmol) was heated under reflux in toluene (5 ml) for 2 h. Hexane (15 ml) was then added and the precipitate formed was filtered off and crystallized from CH_2Cl_2/Et_2O (1/5 ml).

4a. Yield: 0.23 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (d, *J* = 2.1 Hz, 2 H, Ar–H), 6.77 (d, *J* = 2.0 Hz, 2 H, Ar–H), 4.43 (s, 2 H, COD–*CH*), 3.33 [m, 1 H, N(CH_3)*CH*CH_2N], 3.28 (d, *J* = 0.6 Hz, 2 H, COD–*CH*), 3.24 [m, 2 H, N(CH_3)CH*C*H$_2$N], 2.20, 2.19, 2.17, 2.15, 2.12 1.94 (s, 18 H, Ar–CH_3), 1.68 (t, *J* = 1.0 Hz, 4 H, COD–*CH*$_2$), 1.53 (t, *J* = 1.0 Hz 4 H, COD–*CH*$_2$), 1.12 [d, 3 H *J* = 3.0 Hz, N(*CH*$_3$)CHCH$_2$N]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.8 (d, *J* = 48.3 Hz, Rh–C), 146.2, 143.7, 139.4, 139.3, 138.4, 138.0, 128.1, 127.9, 127.6, 126.8, 126.5, 124.7 (Ar–C), 96.9, 66.7 (COD–*CH*), 53.1, 51.8 [N(CH_3)CHCH$_2$N], 31.6, 27.1 (COD–*CH*$_2$), 17.9, 17.8, 17.7, 16.7, 15.6, 15.3 14.0 (Ar–*C*H$_3$, N(CH_3)CHCH$_2$N). Anal. calcd for $C_{30}H_{40}ClN_2Rh$ (M = 567.0): C, 63.55; H, 7.11; Cl,6.25; N, 4.94. Found: C, 63.52; H7.12; Cl,6.22; N, 4.89%.

4c. Yield: 0.22 g, 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 1.9 Hz, 2 H, Ar–H), 7.17 (d, *J* = 1.9 Hz, 2 H, Ar–H), 4.40 (s, 2 H, COD–CH), 3.38–3.36 [m, 2 H, N(CH_3)CHCH(CH_2CH_3)N], 3.25 (d, *J* = 0.6 Hz, 2 H, COD–CH), 2.33 [m, 2 H, N(CH_3)CHCH(CH_2CH_3)N], 2.27, 2.21, 2.19, 2.15, 1.99, 1.97 (s, 18 H, Ar–CH_3), 1.67 (t, *J* = 1.0 Hz 4 H, COD–CH_2), 1.56 (t, *J* = 1.1 Hz, 4 H, COD–CH_2), 1.14–1.10 [m, 6 H N(CH_3)CHCH(CH_2CH_3)N]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.7 (d, *J* = 48.0 Hz, Rh–C), 143.2, 143.0, 140.4, 139.9, 138.7, 138.5, 129.8, 129.5, 127.7, 126.9, 126.7, 124.0 (Ar–C), 96.0, 66.9 (COD–CH), 53.4, 52.0 [N(CH_3)CHCH(CH_2CH_3)N], 31.9, 28.3 (COD–CH_2), 19.8, 19.0, 18.7, 17.7, 17.0, 16.3, 15.3, 14.9, 14.0 [Ar–CH_3, N(CH_3)CHCH(CH_2CH_3)N]. Anal. calcd for $C_{33}H_{48}ClN_2Rh$ (M = 595.1): C, 64.59; H, 7.45; Cl,5.96; N, 4.71. Found: C, 64.62; H7.50; Cl,7.35; N, 4.66%.

4d. Yield: 0.26 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 2.0 Hz, 2 H, Ar–H), 7.33 (d, J = 1.9 Hz, 2 H, Ar–H), 4.45 (s, 2 H, COD–CH), 3.33–3.30 [m, 2 H, N(CH_3)CHCH($CH_2CH_2CH_3$)N], 3.24 (d, J = 0.6 Hz, 2 H, COD–CH), 2.30 [m, 2 H, N(CH_3)CHCH($CH_2CH_2CH_3$)N], 2.19, 2.17, 2.16, 2.15, 2.10, 1.90 (s, 18 H, Ar–CH_3), 1.73 (t, J = 1.0 Hz, 4 H, COD–CH_2), 1.60 (t, J = 1.0 Hz, 4 H, COD–CH_2), 1.23–1.19 [m, 8 H N(CH_3)CHCH($CH_2CH_2CH_3$)N]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.6 (d, J = 48.5 Hz, Rh–C), 144.0, 143.8, 141.3, 140.9, 139.0, 138.0, 129.5, 129.3, 128.0, 127.4, 126.5, 124.9 (Ar–C), 96.4, 67.0 (COD–CH), 52.9, 51.0 [N(CH_3)CHCH($CH_2CH_2CH_3$)N], 31.7, 29.0 (COD–CH_2), 19.6, 19.2, 18.9, 18.7, 17.3, 16.3, 15.4, 14.9, 13.1, 12.9 [Ar–CH_3, N(CH_3)CHCH($CH_2CH_2CH_3$)N]. Anal. calcd for $C_{33}H_{46}ClN_2Rh$ (M = 609.1): C, 65.07; H, 7.61; Cl,5.82; N, 4.60. Found: C, 65.13; H, 7.59; Cl,5.82; N, 4.63%.

4e. Yield: 0.26 g, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J = 1.9 Hz, 4 H, Ar–H), 7.19 (t, J = 1.9 Hz, 2 H, Ar–H), 4.39 (s, 2 H, COD–CH), 3.84 (m, 4 H, NCH_2CH_2N), 3.27 (d, J = 0.6 Hz, 2 H, COD–CH), 2.58, 2.30 (s, 12 H, Ar–CH_3), 1.78 (t, J = 1.0 Hz, 4 H, COD–CH_2), 1.56 (t, J = 1.0 Hz, 4 H, COD–CH_2). ^{13}C NMR 100 MHz ($CDCl_3$): δ 211.8 (d, J = 48.0 Hz, Rh–C) 137.9, 137.7, 134.5, 128.2, 127.2, 126.7 (Ar–C), 96.5, 66.5 (COD–CH), 50.2 (NCH_2CH_2N), 31.6, 27.1 (COD–CH_2), 19.0, 17.4 (Ar–CH_3). Anal. calcd for $C_{27}H_{34}ClN_2Rh$ (M = 524.9): C, 61.78; H, 6.53; Cl,6.75; N, 5.34%. Found: C, 61.83; H, 6.48; Cl,6.66; N, 6.69.

4f. Yield: 0.22 g 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 2 H, Ar–H), 7.02 (s, 2 H, Ar–H), 4.47 (s, 2 H, COD–CH), 3.86 (m, 4 H, NCH_2CH_2N), 3.36 (d, J = 0.6 Hz, 2 H, COD–CH), 2.59, 2.34, 2.31 (s, 18 H, Ar–CH_3), 1.78 (t, J = 1.3 Hz, 4 H, COD–CH_2), 1.56 (t, J = 1.9 Hz, 4 H, COD–CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7 (d, J = 48.0 Hz, Rh–C) 137.9, 136.8, 135.3, 134.1, 128.9, 127.3 (Ar–C), 96.2, 66.5 (COD–CH), 50.3 (NCH_2CH_2N), 31.6, 27.1 (COD–CH_2), 20.0, 18.9, 17.3 (Ar–CH_3). Anal. calcd for $C_{29}H_{38}ClN_2Rh$ (M = 552.9): C, 62.99; H, 6.93; Cl,6.41; N: 5.07%. Found: C, 62.93; H, 6.88; Cl,6.45; N, 5.09.

4g. Yield: 0.18 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 2 H, Ar–H), 7.32 (s, 2 H, Ar–H), 4.54 (s, 2 H, COD–CH), 3.81 (m, 4 H, NCH_2CH_2N), 3.29 (s, 2 H, COD–CH), 2.61, 2.32 (s, 12 H, Ar–CH_3), 1.81 (t, J = 1.3 Hz, 4 H, COD–CH_2), 1.56 (t, J = 1.3 Hz 4 H, COD–CH_2). ^{13}C NMR 100 MHz, $CDCl_3$): δ 213.8 (d, J = 48.1 Hz, Rh–C) 141.3, 137.8, 132.4, 132.0, 130.8, 122.1 (Ar–C), 97.7, 68.1 (COD–CH), 51.4 (NCH_2CH_2N), 32.8, 28.3 (COD–CH_2), 20.2, 18.7 (Ar–CH_3). Anal. calcd for $C_{27}H_{32}Br_2ClN_2Rh$ M = 682.7): C: 47.50, H: 4.72, Cl,5.19; N: 4.10%. Found: C, 47.53; H, 4.78; Cl,5.25; N, 4.19%.

4h. Yield: 0.17 g, 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 7.9 Hz, 2 H, Ar–H), 7.32 (d, J = 7.9 Hz, 2 H, Ar–H), 7.26 (s, 2 H, Ar–H), 4.46 (s, 2 H, COD–CH), 3.86 (m, 4 H, NCH_2CH_2N), 3.22 (s, 2 H, COD–CH), 2.40, 2.23 (s, 12 H, Ar–CH_3), 1.81 (t, J = 1.3 Hz, 4 H, COD–CH_2), 1.75 (t, J = 1.4 Hz 4 H, COD–CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.2 (d, J = 49.0 Hz, Rh–C) 138.1, 138.0, 134.4, 131.6, 131.0, 127.6 (Ar–C), 97.3, 66.9 (COD–CH), 52.6 (NCH_2CH_2N), 31.6, 27.1 (COD–CH_2), 19.5, 18.7 (Ar–CH_3). Anal. calcd for $C_{27}H_{34}ClN_2Rh$ (M = 524.9): C, 61.78; H, 6.53; Cl,6.75; N, 5.34%. Found: C, 61.73; H, 6.70; Cl,6.70; N, 5.29%.

4i. Yield: 0.24 g, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 7.9 Hz, 2 H, Ar–H), 7.32 (d, J = 7.9 Hz, 2 H, Ar–H), 7.26 (s, 2 H, Ar–H), 4.46 (s, 2 H, COD–CH), 3.79 (m, 4 H, NCH_2CH_2N), 3.22 (s, 2

H, COD–CH), 2.53, 2.07 (s, 12 H, Ar–CH_3), 1.81 (t, J = 1.3 Hz, 4 H, COD–CH_2), 1.75 (t, J = 1.4 Hz, 4 H, COD–CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.5 (d, J = 48.0 Hz, Rh–C) 140.1, 136.8, 136.6, 131.1, 129.6, 120.9 (Ar–C), 97.3, 66.9 (COD–CH), 50.2 (NCH_2CH_2N), 31.6, 27.1 (COD–CH_2), 19.0, 17.3 (Ar–CH_3). Anal. calcd for $C_{27}H_{33}Cl_3N_2Rh$ (M = 593.8): C, 54.61, H, 5.43, Cl,17.91; N, 4.72%. Found: C, 54.63; H, 5.55; Cl,17.95; N, 4.83%.

Synthesis of [RhCl(CO)$_2$(NHC)] Derivatives, 5

RhCl(NHC)(COD), 4 (0.25 mmol) was disolved in 5 ml dichloromethane. Carbon monoxide was bubbled through the solution for 30 min. A color change from orange to pale was observed. The reaction mixture was stirred at room temparature for 2 h. Pentane was added to the mixture which was filtered.

5a. Yield: 0.12 g, 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (d, J = 2.1 Hz, 2 H, Ar–H), 6.72 (d, J = 2.1 Hz, 2 H, Ar–H), 3.43 [m, 1 H, N(CH_3)CHCH_2N], 3.30 [m, 2 H, N(CH_3)CHCH_2N], 2.27, 2.23, 2.21, 2.19, 2.17, 2.13 (s, 18 H, Ar–CH_3), 1.16 [d, 3 H, J = 2.8 Hz, N(CH_3)CHCH_2N]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.8 (d, J = 41.3 Hz, Rh–C), 185.5 (d, $^1J_{103}$Rh = 53,2 Hz, Rh–CO), 182.7 (d, $^1J_{103}$Rh = 74.6 Hz, Rh–CO), 146.3, 144.7, 140.0, 139.8, 138.7, 128.1 (Ar–C), 53.8, 51.3 (N(CH_3)CHCH_2N), 18.5, 18.3, 17.7, 17.3, 16.5, 16.0, 14.4 (Ar–CH_3, N(CH_3)CHCH_2N). Anal. calcd for $C_{21}H_{23}ClN_2O_2Rh$ (M = 514.9): C, 55.99; H, 5.48; Cl,6.89; N, 5.44. Found: C, 55.90; H, 5.50; Cl,6.85; N, 5.46%. IR (CH_2Cl_2): υ = 2079, 1995 (CO) cm^{-1}.

5c. Yield: 0.13 g, 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (d, *J* = 2.0 Hz, 2 H, Ar–H), 6.90 (d, *J* = 1.9 Hz, 2 H, Ar–H), 3.86–3.84 [m, 2 H, N(CH_3)*CHCH*(CH_2CH_3)N], 2.33 [m, 2 H, N(CH_3)CHCH(*CH_2*CH_3)N], 2.20, 2.19, 2.18, 2.13, 2.07, 2.03, (s, 18 H, Ar–CH_3), 1.23–1.20 [m, 6 H N(*CH_3*)CHCH(CH_2*CH_3*)N]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.0 (d, *J* = 41.3 Hz, Rh–C), 185.0 (d, $^1J_{103}$Rh = 53,1 Hz, Rh–CO), 182.3 (d, $^1J_{103}$Rh =74.5 Hz, Rh–CO), 142.1, 141.9, 141.0, 139.7, 138.9, 138.7, 135.8, 134.4 (Ar–C), 53.2, 52.7 [N(CH_3)*CHCH*(CH_2CH_3)N], 20.1, 19.8, 19.6, 18.9, 17.9, 17.8, 16.5, 14.9, 14.1 [Ar–CH_3, N(CH_3)CHCH(*CH_2*CH_3)N]. Anal. calcd for $C_{26}H_{32}ClN_2O_2Rh$ (M = 542.9): C, 57.52; H, 5.94; Cl,6.53; N, 5.16. Found: C, 57.60; H, 5.91; Cl,6.55; N, 5.16%. IR (CH_2Cl_2): υ = 2077, 1993 (CO) cm^{-1}.

5d. Yield: 0.13 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 1.9 Hz, 2 H, Ar–H), 7.19 (d, *J* = 1.9 Hz, 2 H, Ar–H), 3.33–3.30 [m, 2 H, N(CH_3)*CHCH*($CH_2CH_2CH_3$)N], 2.33 [m, 2 H, N(CH_3)CHCH(*CH_2*CH_2CH_3)N], 2.23, 2.21, 2.18, 2.16, 2.15, 2.13 (s, 18 H, Ar–CH_3), 1.27–1.25 [m, 8 H N(*CH_3*)CHCH(CH_2*CH_2*CH_3)N]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.7 (d, *J* = 41.7 Hz, Rh–C), 185.5 (d, $^1J_{103}$Rh = 52,8 Hz, Rh–CO), 183.2 (d, $^1J_{103}$Rh = 74.7 Hz, Rh–CO), 144.5, 144.0, 142.0, 141.0, 138.7, 130.9, 130.2, 128.0 (Ar–C), 52.3, 51.9 [N(CH_3)*CHCH*($CH_2CH_2CH_3$)N], 20.0, 19.8, 18.7, 18.3, 17.9, 16.1, 15.7, 15.0, 14.1, 13.7 [Ar–CH_3, N(CH_3)CHCH(*CH_2*CH_2CH_3)N]. Anal. calcd for $C_{27}H_{34}ClN_2O_2Rh$ (M = 556.9): C, 58.23; H, 6.15; Cl,6.37; N, 5.03. Found: C, 58.17; H, 6.09; Cl,6.38; N, 5.06%. IR (CH_2Cl_2): υ = 2076, 1993 (CO) cm^{-1}.

5e. Yield: 0.11 g, 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, J = 0.6 Hz, 4 H, Ar–H), 7.17 (d, J = 2.0 Hz, 2 H, Ar–H), 4.04 (s, 4 H, NCH_2CH_2N), 2.48 (s, 12 H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.7 (d, J = 41.0 Hz, Rh–C), 185.1 (d, $^1J_{103}$Rh = 53,4 Hz, Rh–CO), 182.9 (d, $^1J_{103}$Rh =74.7 Hz, Rh–CO), 139.1, 137.6, 131.1, 128.2 (Ar–C), 51.7 (NCH_2CH_2N), 19.1 (Ar–CH_3). Anal. calcd for $C_{21}H_{22}ClN_2O_2Rh$ (M = 472.8): C, 53.35; H, 4.69; Cl,7.50; N, 5.93. Found: C, 53.39; H, 4.63; Cl,7.55; N, 5.83%. IR (CH_2Cl_2): υ = 2084, 1996 (CO) cm^{-1}.

5f. Yield: 0.12 g, 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 (s, 4 H, Ar–H), 3.79 (s, 4 H, NCH_2CH_2N), 2.41 (s, 12 H, Ar–CH_3), 2.37 (s, 6 H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.8 (d, J = 41.3 Hz, Rh–C), 185.0 (d, $^1J_{103}$Rh = 52,5 Hz, Rh–CO), 182.8 (d, $^1J_{103}$Rh = 73.3 Hz, Rh–CO), 142.5, 137.9, 137.0, 129.4 (Ar–C), 51.3 (NCH_2CH_2N), 19.0 (Ar–CH_3). Anal. calcd for $C_{23}H_{26}ClN_2O_2Rh$ (M = 500.8): C, 55.16; H, 5.23; Cl,7.08; N, 5.59. Found: C, 55.19; H, 5.18; Cl,7.12; N, 5.58%. IR (CH_2Cl_2): υ = 2081, 1996 (CO) cm^{-1}.

5g. Yield: 0.15 g, 93%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (s, 4 H, Ar–H), 3.93 (s, 4 H, NCH_2CH_2N), 2.48 (s, 12 H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.7 (d, J = 42.0 Hz, Rh–C), 184.7 (d, $^1J_{103}$Rh = 53,1 Hz, Rh–CO), 182.9 (d, $^1J_{103}$Rh = 74.0 Hz, Rh–CO), 142.0, 137.8, 137.0, 128.0 (Ar–C), 52.4 (NCH_2CH_2N), 19.4 (Ar–CH_3). Anal. calcd for $C_{21}H_{20}Br_2ClN_2O_2Rh$ (M = 630.6): C, 40.00; H, 3.20; Cl,5.62; N, 4.44. Found: C, 40.09; H, 3.14; Cl,5.58; N, 4.46%. IR (CH_2Cl_2): υ = 2092, 1994 (CO) cm^{-1}.

5h. Yield: 0.10 g, 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 1.9 Hz, 2 H, Ar–H), 7.17 (d, J = 1.9 Hz, 2 H, Ar–H), 6.95 (s, 2 H, Ar–H), 3.81 (s, 4 H, NCH_2CH_2N), 2.27 (s, 6 H, Ar–CH_3), 2.21 (s, 6 H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.8 (d, J = 41.0 Hz, Rh–C), 184.6 (d, $^1J_{103}$Rh = 52,9 Hz, Rh–CO), 182.5 (d, $^1J_{103}$Rh = 73.7 Hz, Rh–CO), 139.4, 137.6, 137.0, 131.9, 127.5, 123.1 (Ar–C), 51.7 (NCH_2CH_2N), 19.9, 19.0 (Ar–CH_3). Anal. calcd for $C_{21}H_{22}ClN_2O_2Rh$ (M = 472.8): C, 53.35; H, 4.69; Cl,7.50; N, 5.93. Found: C, 53.24; H, 4.73; Cl,7.45; N, 5.91%. IR (CH_2Cl_2): υ = 2103, 1999 (CO) cm^{-1}.

5i. Yield: 0.11 g, 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 4 H, Ar–H), 3.88 (s, 4 H, NCH_2CH_2N), 2.51 (s, 12 H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.8 (d, J = 42.0 Hz, Rh–C), 185.1 (d, $^1J_{103}$Rh = 53,3 Hz, Rh–CO), 182.7 (d, $^1J_{103}$Rh = 74.4 Hz, Rh–CO), 143.8, 138.0, 137.6, 128.9 (Ar–C), 51.7 (NCH_2CH_2N), 18.2 (Ar–CH_3). Anal. calcd for $C_{21}H_{20}Cl_3N_2O_2Rh$ (M = 541.6): C, 46.57; H, 3.72; Cl,19.64; N, 5.17. Found: C, 46.50; H, 3.69; Cl,19.65; N, 5.13%. IR (CH_2Cl_2): υ = 2080, 1997 (CO) cm^{-1}.

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), the aromatic aldehyde (4.9 mmol), diethyleneglycol di-*n*-butyl ether (0.6 mmol, internal standard), rhodium–carbene catalyst (1 mol%) and *N*,*N*-dimethylformamide (15 ml) were introduced into a Schlenk tube and then water (5 ml) was added. The resulting mixture was heated for 4 h at 80 °C under an argon atmosphere, cooled to ambient temperature and extracted with ethyl acetate (30 ml). After drying over $MgSO_4$ the organic phase was evaporated. The conversion was monitored by gas chromatography.

Supporting information

Supporting information may be found in the online version of this article.

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