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# Symmetric and dissymmetric *N*-heterocyclic carbene rhodium(I) complexes: a comparative study of their catalytic activities in transfer hydrogenation reaction

Süleyman Gülcemal*

**Six new [RhBr(NHC)(cod)] (NHC = *N*-heterocyclic carbene; cod = 1,5-cyclooctadiene) type rhodium complexes (4–6) have been prepared by the reaction of $[Rh(\mu\text{-}OMe)(cod)]_2$ with a series of corresponding imidazoli(in)ium bromides (1–3) bearing mesityl (Mes) or 2,4,6-trimethylbenzyl ($CH_2Mes$) substituents at $N^1$ and $N^3$ positions. They have been fully characterized by $^1H$, $^{13}C$ and heteronuclear multiple quantum correlation NMR analyses, elemental analysis and mass spectroscopy. Complexes of type $[(NHC)RhBr(CO)_2]$ (NHC = imidazol-2-ylidene) (7b–9b) were also synthesized to compare σ-donor/π-acceptor strength of NHC ligands. Transfer hydrogenation (TH) reaction of acetophenone has been comparatively studied by using complexes 4–6 as catalysts. The symmetrically $CH_2Mes$-substituted rhodium complex bearing a saturated NHC ligand (5a) showed the highest catalytic activity for TH reaction. Copyright © 2012 John Wiley & Sons, Ltd.**

**Keywords:** *N*-heterocyclic carbene; rhodium; transfer hydrogenation

## Introduction

Rhodium complexes of *N*-heterocyclic carbene (NHC) ligands have been the focus of intense research in organometallic chemistry and homogeneous catalysis,[1] after the first efficient catalytic applications of these complexes reported by Lappert and Maskell.[2] The electronic and steric parameters of NHC complexes can be modified easily, and they have greater stability toward air, moisture and heating when compared with phosphine analogues.[3] NHCs are strongly bound to the metal, which avoids decomposition to free and inactive metal under catalytic conditions in many cases.[4] Thus NHC–rhodium complexes have been employed as catalysts for number of catalytic applications such as hydrogenation, transfer hydrogenation (TH), hydrosilylation and hydroformylation.[5]

NHCs exhibit good σ-donor and weak π-acceptor electronic properties.[6] Measurement of carbonyl stretching frequencies in $[(NHC)Rh(X)(CO)_2]$ (X = halogen) complexes with infrared (IR) spectroscopy can be used to compare donor properties of NHC ligands, which are important for homogeneous catalysis.[7] These electronic properties can be modified by changing the substituents at the 4,5-position of imidazol(in)e backbone or by adding different substituents on nitrogen atoms of heterocycle.[8]

In 2009, Herrmann's group prepared [(NHC)Ir(X)(cod)] (cod = 1, 5-cyclooctadiene) type iridium(I) complexes and investigated the effect of different NHC ligands on catalytic activity in the TH reaction.[9] They observed that weaker donor strength of the NHC ligand seems to increase the complex activity by both shortening the initiation time and accelerating the catalytic reaction when acetophenone is the substrate. However, no significant difference was observed when the NHC was 1,3-dimethylimidazol-2-ylidene or 1,3-dimethylimidazolin-2-ylidene (IR data confirm the donor strength of these two ligands being quite similar). As a result, it was found that steric and electronic effects influence the catalytic activity considerably.

Nolan's group reported that whereas $[(IMes)Ir(py)(cod)]^+PF_6^-$ complex requires 4.5 h for total conversion of cyclohexanone to cyclohexyl alcohol, saturated $[(SIMes)Ir(py)(cod)]^+PF_6^-$ complex requires a longer reaction time (6 h).[10]

Practically almost all catalytic studies have been devoted to saturated imidazolin-2-ylidene and unsaturated imidazol-2-ylidene bearing symmetric aryl or benzyl substituents, while related dissymmetrically substituted imidazol(in)-2-ylidenes have not received sufficient attention.[11] Therefore, a comparative experimental study of NHCs with Mes and $CH_2Mes$ substituents on the N atoms is presented.

## Results and Discussion

The NHC ligand precursors used in this study fall into three general types, featuring different substituents: symmetric $N^1$, $N^3$-dimesityl (Scheme 1), $N^1$,$N^3$-dibenzyl and dissymmetric $N^1$-benzyl-$N^3$-mesityl (Scheme 2) on the $N^1$ and $N^3$ atoms.

The salt **2a** was synthesized using a published procedure with slight modification (Scheme 2, route i).[12] Its unsaturated analogue **2b** was prepared by addition of 2 equiv. of 2,4,6-trimethylbenzyl bromide to a solution of imidazole in DMF without additional base

* *Correspondence to: Süleyman Gülcemal, Department of Chemistry, Ege University, İzmir, Turkey. E-mail: suleyman.gulcemal@ege.edu.tr*

*Dedicated to Prof. Bekir Çetinkaya for his great contribution in the field of N-heterocyclic carbene chemistry since 1971.*

*Department of Chemistry, Ege University, İzmir, Turkey*


**1a** (SIMes.HBr) **1b** (IMes.HBr)

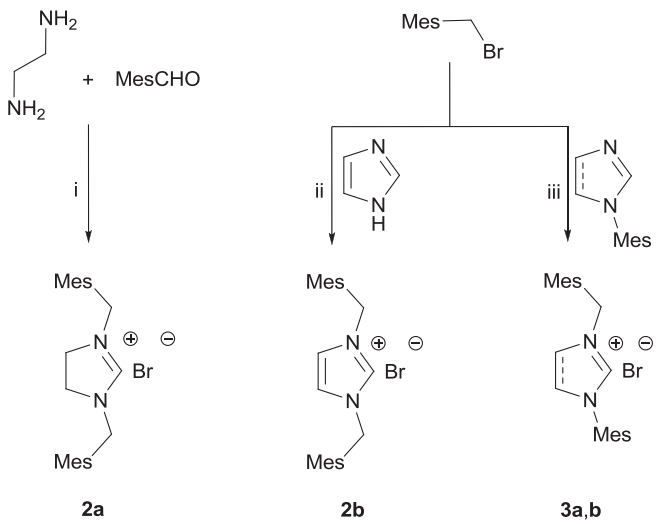
**Scheme 1.** Saturated (a) and unsaturated (b) dimesitylimidzol(in)ium salts.

(Scheme 2, route ii). In the $^{1}$H NMR spectra the NC*H*N$^{+}$ protons of **2a** and **2b** appear at 9.30 and 9.70 ppm respectively. $^{13}$C NMR shifts of NCHN$^{+}$ appear at 157.7 and 140.0 ppm respectively.

Dissymmetric imidazol(in)ium bromide salts (**3a**, **b**) were obtained in almost quantitative yield by quaternization of 1-mesitylimidazoline[13] or 1-mesitylimidazole[14] in toluene with 2,4,6-trimethylbenzyl bromide (Scheme 2). These salts are air stable and colorless solids. The $^{1}$H and $^{13}$C NMR spectra of these salts exhibit characteristic downfield signals. In the $^{1}$H NMR spectrum, the NC*H*N$^{+}$ protons of **3a** and **3b** appear at 9.13 and 10.16 ppm, while the $^{13}$C NMR shifts of NCHN$^{+}$ appear at 158.2 and 141.2 ppm respectively.

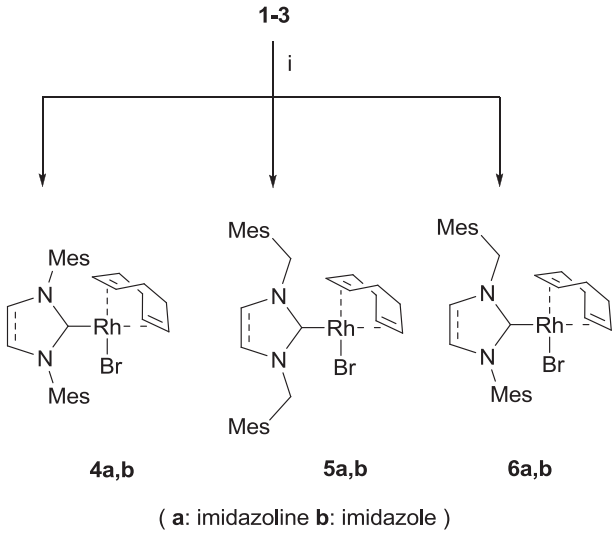
All the new [(NHC)RhBr(cod)] complexes were obtained through reaction of two equivalents imidazol(in)ium salts (**1–3**) with [Rh(μ-OMe)(cod)]$_2$ in refluxing dichloromethane. Complexes **4–6** were obtained in high yield as air-stable orange solids (Scheme 3).

The identity of complexes **4–6** was confirmed by $^{1}$H, $^{13}$C, heteronuclear multiple quantum correlation (HMQC) NMR, elemental analysis and mass spectroscopy. The characteristic downfield signals for the NC*H*N$^{+}$ protons of the imidazol(in)ium salts disappeared in the $^{1}$H NMR spectra of complexes **4–6**. These complexes exhibit $^{13}$C chemical shifts and coupling constants that are comparable to those of other reported NHC–rhodium(I) complexes.[8,11,15] $^{13}$C chemical shifts showed that $C_{carbene}$ is substantially deshielded. The carbon atoms in the two cyclooctadiene double bonds are coupled with the rhodium centre




**2a** **2b** **3a,b**

**Scheme 2.** Synthesis of imidazol(in)ium salts: (i) PhMe, r.t., 4 h; MeOH, $NaBH_4$, r.t., overnight; $CH(OEt)_3$, $NH_4Br$, 100 °C, 6 h. (ii) DMF, 100 °C, overnight. (iii) PhMe, 80 °C, 1 h.




**4a,b** **5a,b** **6a,b**

( **a**: imidazoline **b**: imidazole )

**Scheme 3.** Synthesis of [(NHC)RhBr(cod)] complexes: (i) [Rh(OMe)(cod)]$_2$, $CH_2Cl_2$, reflux, 24 h.

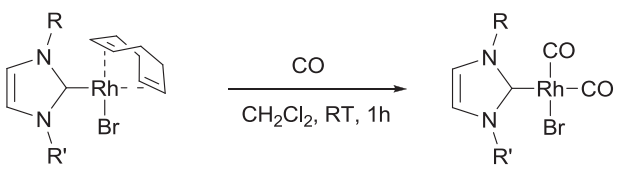
differently ($J_{Rh-C}$ = ~6.8 and ~14.5 Hz), which is consistent with their position *trans* to NHC and the Br atom, respectively.

The corresponding carbonyl substituted NHC–rhodium complexes, [(NHC)RhBr(CO)$_2$], **7b**, **8b** and **9b** are obtained by passing carbon monoxide through a dichloromethane solution of the [(NHC)RhBr(cod)] complexes, **4b**, **5b**, and **6b** at r.t. (Scheme 4). These reactions resulted in almost quantitative replacement of cod ligand by CO ligands. These complexes were produced in order to compare electronic properties of corresponding NHC ligand, which could be done by measuring the carbonyl stretching frequencies of [(NHC)RhBr(CO)$_2$] complexes with IR.

The *cis* conformation of the CO ligands in complexes **7b**, **8b**, and **9b** was confirmed by IR and NMR spectroscopy. The IR spectra exhibit two strong $\nu_{CO}$ bands in each complex. IR data confirm the donor strength of the NHC ligands in the complexes being quite similar. $^{13}$C NMR spectra exhibit three doublets around 175, 183 and 186 ppm with the coupling constant of 43, 76 and 53 Hz for the two CO and $C_{carbene}$ ligands respectively.

The relevant data for the characterization of all ligand precursors (**1–3**), cod complexes (**4–6**) and carbonyl complexes (**7b–9b**) are complied in Table 1 for the sake of comparison.

TH reactions require typically a hydrogen donor such as 2-propanol together with a strong base and an Ru, Rh or Ir as catalyst,[16] and is preferred for large-scale industrial use




**4b, 5b, 6b**

**7b:** R=R'=Mes
**8b:** R=R'=$CH_2$Mes
**9b:** R=;$CH_2$Mes; R'=Mes

**Scheme 4.** Synthesis of [(NHC)RhBr(CO)$_2$] complexes.

**Table 1.** Spectroscopic data for compounds **1–6** and **7b–9b**

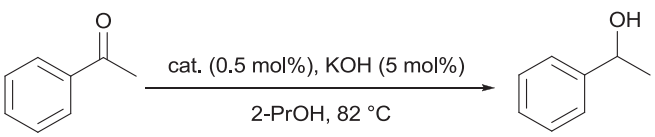
| Compound | $\delta$ $C_2$-*H* | $\delta$ $C_2$-Rh | $\nu_{av}$-CO ($cm^{-1}$) |
|---|---|---|---|
| **1a** | 9.18 | — | — |
| **1b** | 9.20 | — | — |
| **2a** | 9.30 | — | — |
| **2b** | 9.70 | — | — |
| **3a** | 9.13 | — | — |
| **3b** | 10.16 | — | — |
| **4a** | — | 212.7 | — |
| **4b** | — | 183.7 | — |
| **5a** | — | 214.5 | — |
| **5b** | — | 182.3 | — |
| **6a** | — | 212.3 | — |
| **6b** | — | 180.3 | — |
| **7b** | — | 185.3 | 2038.2 |
| **8b** | — | 186.5 | 2039.6 |
| **9b** | — | 186.1 | 2039.3 |

in the hope of developing a greener process by reducing waste production and energy use, and lowering toxicity.[17]

Complexes **4–6** were tested as catalysts for transfer hydrogenation of acetophenone to 1-phenylethanol using 2-propanol as hydrogen donor in the presence of KOH (Scheme 5). The catalytic experiments were carried out using 4.0 mmol of acetophenone, 0.02 mmol (0.5 mol%) of NHC–rhodium complexes (**4–6**), 0.2 mmol KOH and 20 ml 2-propanol, with a catalyst/base/substrate ratio of 0.5:5:100. The catalyst was added to a solution of 2-propanol containing KOH, which was kept at 82 °C for 30 min. and acetophenone was added to this solution. Percentage conversion was calculated by comparing the methyl proton signals of acetophenone (s, $\delta$ 2.60 ppm) and 1-phenylethanol (d, $\delta$ 1.50 ppm, $J = 6.8$ Hz) in the $^1$H NMR spectrum of the crude product in $CDCl_3$ and the time-dependent conversions were followed (Fig. 1).

The activity of complexes **4–6** largely depends on the nature of *N*-substituents and decreases in the order **5a** > **5b** ~ **6a** > **6b** ~ **4a** ~ **4b**, indicating that the most bulky **4a** and **4b** show the most noticeable activation period and reach a maximum yield of ~50% after 2 h. As Herrmann and coworkers suggested, the introduction of an α-hydrogen on the nitrogen substituent enhances the activity.[9] The flexibility of the benzyl substituent may also contribute to the catalytic performance of the complexes.

In this series of compounds, it has been observed that the greatest efficiency in rate was achieved with dibenzyl substituent on N atoms of imidazolin-2-ylidene. This feature of the reaction was attributed to the flexibility of the $CH_2$Mes substituents versus rigidity of Mes substituents. Within these frameworks it has been demonstrated that the catalytic efficiency is influenced by the type of substituents attached to the nitrogen atoms and to a lesser extent by the 4,5-




**Scheme 5.** TH of acetophenone

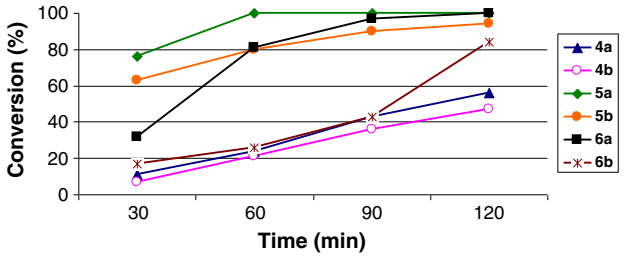



**Figure 1.** Time dependence of the catalytic transfer hydrogenation of acetophenone.

position of the ring. But for the complexes **6a** and **6b** bearing dissymmetrically substituted NHC ligand, the catalytic activity differs significantly during the first 90 min. Saturated NHC-bearing complex **6a** shows a better initiation time than unsaturated NHC-bearing complex **6b**.

## Conclusions

In this report, a comparative study on the efficiencies of imidazol(in)-2-ylidenes bearing 2,4,6-trimethylphenyl (Mes) or 2,4,6-trimethylbenzyl ($CH_2$Mes) substituents on nitrogen atoms was investigated. It is clear that the introduction of the $CH_2$Mes group to the nitrogen atoms increased TH performance. The 4,5-position of the imidazole ring did not show a dramatic effect.

## Experimental

All manipulations were performed in air. The solvents were used as received. The reagents were purchased from Sigma-Aldrich, Merck, Alfa Aesar and Acros Organics. 1-Mesitylimidazoline,[13] 1-mesitylimidazole,[14] $N^1$,$N^3$-(dimesityl)imidazolinium bromide (SIMes.HBr)[18], $N^1$,$N^3$-(dimesitylim)idazolium bromide (IMes.HBr)[19] and [Rh(μ-OMe)(cod)]$_2$[20] were prepared according to the published procedures. $^1$H, $^{13}$C and HMQC NMR spectra were recorded with a Varian AS 400 Mercury instrument. As solvent, $CDCl_3$ was employed. Chemical shifts ($\delta$) are given in ppm and coupling constants ($J$) in Hz. FT-IR spectra were recorded on a PerkinElmer Spectrum 100 series. Elemental analyses were performed on a PerkinElmer PE 2400 elemental analyzer. Mass spectra experiments were conducted on Bruker HCT Ultra ion trap mass spectrometer.

### Preparation of Imidazol(in)ium Salts

*Synthesis of **2a***

A mixture of ethylenediamine (0.600 g, 10 mmol) and mesitylaldehyde (2.96 g, 20 mmol) was stirred in toluene (15 ml) at r.t. for 4 h. Solvent was then removed *in vacuo* and MeOH (15 ml) was added to the resulting white solid. $NaBH_4$ (1.76 g, 40 mmol) was added with portions over 1 h at r.t. and the mixture was stirred overnight. MeOH was then removed *in vacuo*, and the residue was dissolved in $Et_2O$ (20 ml) and extracted with $H_2O$ (3 × 10 ml). The organic layer was separated and dried with $Na_2SO_4$. The solvent was removed and to the resulting diimine triethylorthoformate (4.45 g, 30 mmol) and $NH_4Br$ (0.980 g, 10 mmol) were added, and stirred for 6 h. The excess of

triethylorthoformate was removed *in vacuo*; the resulting white solid was dissolved in $CH_2Cl_2$ (5 ml) and precipitated with $Et_2O$ (25 ml). The white solid was filtered and dried. Yield: 3.90 g (86%). $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 9.30 (s, 1 H, NC*H*N$^+$), 6.77 (s, 4 H, C$H_{arom}$), 4.78 (s, 4 H, Mes-C$H_2$-N-), 3.73 (s, 4 H, -N-C$H_2$C$H_2$-N-), 2.25 (s, 6 H, Ar-C$H_3$), 2.16 (s, 3 H, Ar-C$H_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 157.7 (NCHN$^+$), 139.2 (Ar-*C*), 138.0 (Ar-*C*), 129.7 (Ar-*C*), 125.5 (Ar-*C*), 48.1 (Mes-$CH_2$-N-), 46.6 (-N-$CH_2CH_2$-N-), 21.1 (Ar-$CH_3$), 20.3 (Ar-$CH_3$). Anal. Calcd for $C_{23}H_{31}BrN_2$: C, 66.50; H, 7.52; N, 6.74. Found: C, 66.21; H, 7.57; N, 6.72. MS (ESI$^+$): *m/z* 335.4 [M − Br]$^+$, calcd 335.5.

*Synthesis of* ***2b***

A mixture of 2,4,6-trimethylbenzyl bromide (2.14 g, 10 mmol) and imidazole (0.340 g, 5 mmol) was stirred in DMF (10 ml) at 100 °C overnight. It was then cooled to r.t. and the solvent was removed *in vacuo*. The resulting white solid was dissolved in $CH_2Cl_2$ (3 ml) and precipitated with $Et_2O$ (15 ml). The white solid was filtered and dried. Yield: 1.95 mg (92%). $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 9.70 (s, 1 H, NC*H*N$^+$), 6.85 (s, 2 H, -N-C*HCH*-N-), 6.75 (s, 4 H, C$H_{arom}$), 5.42 (s, 4 H, Mes-C$H_2$-N-), 2.12 (s, 12 H, Ar-C$H_3$), 2.11 (s, 6 H, Ar-C$H_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 140.0 (NCHN$^+$), 138.2 (Ar-*C*), 136.2 (Ar-*C*), 130.0 (Ar-*C*), 125.5 (Ar-*C*), 121.3 (-N-*C*H*C*H-N-), 48.3 (Mes-$CH_2$-N-), 21.3 (Ar-$CH_3$), 20.0 (Ar-$CH_3$). Anal. Calcd for $C_{23}H_{29}BrN_2$: C, 66.82; H, 7.07; N, 6.78. Found: C, 66.85; H, 7.04; N, 6.82. MS (ESI$^+$): *m/z* 333.2 [M − Br]$^+$, calcd 333.5.

*Synthesis of* ***3a***

To a solution of 1-mesitylimidazoline (5 mmol, 0.942 g) in toluene (10 ml), 2,4,6-trimethylbenzyl bromide (5 mmol, 1.07 g) was added. The solution stirred at 80 °C for 1 h. The white solid that separated out after cooling to r.t. was filtered off and washed with diethyl ether (20 ml). The product was recrystallized from $CH_2Cl_2$/$Et_2O$. Yield: 1.85 g (92%). $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 9.13 (s, 1 H, NC*H*N$^+$), 6.78 (s, 2 H, C$H_{arom}$), 6.77 (s, 2 H, C$H_{arom}$), 5.05 (s, 2 H, Mes-C$H_2$-N-), 4.05–4.11 (m, 4 H, -N-C$H_2$C$H_2$-N-), 2.28 (s, 6 H, Ar-C$H_3$ *ortho*), 2.18 (s, 6 H, Ar-C$H_3$ *ortho*), 2.17 (s, 3 H, Ar-C$H_3$ *para*), 2.15 (s, 3 H, Ar-C$H_3$ *para*). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 158.2 (NCHN$^+$), 140.3 (Ar-*C*), 139.2 (Ar-*C*), 138.2 (Ar-*C*), 135.4 (Ar-*C*), 130.8 (Ar-*C*), 130.1 (Ar-*C*), 130.0 (Ar-*C*), 125.6 (Ar-*C*), 51.4 (Mes-$CH_2$-N-), 48.7 (-N-$CH_2CH_2$-N-), 46.9 (-N-$CH_2CH_2$-N-), 21.1 (Ar-$CH_3$), 20.4 (Ar-$CH_3$), 18.3 (Ar-$CH_3$). Anal. Calcd for $C_{22}H_{29}BrN_2$: C, 65.83; H, 7.28; N, 6.98. Found: C, 65.86; H, 7.24; N, 6.99. MS (ESI$^+$): *m/z* 321.3 [M-Br]$^+$, calcd 321.5.

*Synthesis of* ***3b***

The salt was synthesized with 1-mesitylimidazole (5 mmol, 0.931 g) by a similar method to that used for **2a**. Yield: 1.90 g (95%). $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 10.16 (s, 1 H, NC*H*N$^+$), 7.32 (s, 1 H, -N-*C*HCH-N-), 7.06 (s, 1 H, -N-CH*C*H-N-), 6.79 (s, 2 H, C$H_{arom}$), 6.75 (s, 2 H, C$H_{arom}$), 5.74 (s, 2 H, Mes-$CH_2$-N-), 2.15 (s, 9 H, Ar-C$H_3$), 2.12 (s, 3 H, Ar-C$H_3$), 1.87 (s, 6 H, Ar-C$H_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 141.2 (NCHN$^+$), 139.8 (Ar-*C*), 138.1 (Ar-*C*), 137.3 (Ar-*C*), 134.2 (Ar-*C*), 130.8 (Ar-*C*), 130.0 (Ar-*C*), 129.9 (Ar-*C*), 125.8 (Ar-*C*), 124.4 (-N-*C*HCH-N-), 121.9 (-N-CH*C*H-N-), 48.5 (Mes-$CH_2$-N-), 21.1 (Ar-$CH_3$), 20.0 (Ar-$CH_3$), 17.7 (Ar-$CH_3$). Anal. Calcd for $C_{22}H_{27}BrN_2$: C, 66.16; H, 6.81; N, 7.01. Found: C, 66.14; H, 6.76; N, 6.97. MS (ESI$^+$): *m/z* 319.2 [M − Br]$^+$, calculated 319.5.

**General Procedure for Preparation of the [(NHC)RhBr(cod)] Complexes**

Imidazol(in)ium salt (1.0 mmol) was dissolved in 10 ml $CH_2Cl_2$ and [Rh(μ-OMe)(cod)]$_2$ (0.5 mmol, 0.242 g) was added to the solution. The mixture was refluxed for 24 h. The solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (eluent: $CH_2Cl_2$) to give pure complex as an orange solid. The following complexes (**4–6**) were synthesized according to this procedure.

*Complex* ***4a***

Yield: 0.480 g (80%). $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.01 (s, 2 H, C$H_{arom}$), 6.97 (s, 2 H, C$H_{arom}$), 4.59 (br, 2 H, COD-C*H*), 389–3.86 and 3.83–3.81 (m, 4 H, -N-C$H_2CH_2$-N-), 3.46 (br, 2 H, COD-C*H*), 2.61 (s, 6 H, Ar-C$H_3$), 2.34 (s, 12 H, Ar-C$H_3$), 1.80–1.75 (m, 4 H, COD-C$H_2$), 1.56–1.48 (m, 4 H, COD-C$H_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 212.7 (d, $J_{Rh-Carbene}$ = 48.4 Hz, $C_{carbene}$), 138.4 (Ar-*C*), 138.1 (Ar-*C*), 136.6 (Ar-*C*), 135.5 (Ar-*C*), 130.2 (Ar-*C*), 128.7 (Ar-*C*), 96.9 (d, $J_{Rh-C}$ = 6.9 Hz, COD-*C*H), 68.8 (d, $J_{Rh-C}$ = 14.6 Hz, COD-*C*H), 32.7 (COD-$CH_2$), 28.7 (COD-$CH_2$), 21.3 (Ar-$CH_3$), 21.0 (Ar-$CH_3$), 18.7 (Ar-$CH_3$). Anal. Calcd for $C_{29}H_{38}BrN_2Rh$: C, 58.30; H, 6.41; N, 4.69. Found: C, 58.22; H, 6.46; N, 4.72. MS (ESI$^+$): *m/z* 517.2 [M − Br]$^+$, calcd 517.5.

*Complex* ***4b***

Yield: 0.549 g (92%). $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.03 (s, 2 H, C$H_{arom}$), 7.00 (s, 2 H, C$H_{arom}$), 6.94 (m, 4 H, -N-C*HCH*-N-), 4.50 (br, 2 H, COD-C*H*), 3.29 (br, 2 H, COD-C*H*), 2.39 (s, 6 H, Ar-C$H_3$), 2.37 (s, 6 H, Ar-C$H_3$), 2.13 (s, 6 H, Ar-C$H_3$), 1.84–1.82 (m, 4 H, COD-C$H_2$), 1.54–1.52 (m, 4 H, COD-C$H_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 183.7 (d, $J_{Rh-Carbene}$ = 52.9 Hz, $C_{carbene}$), 138.8 (Ar-*C*), 137.7 (Ar-*C*), 136.5 (Ar-*C*), 134.6 (Ar-*C*), 129.9 (-N-CHCH-N-), 128.4 (-N-CHCH-N-), 96.2 (d, $J_{Rh-C}$ = 7.8 Hz, COD-*C*H), 68.1 (d, $J_{Rh-C}$ = 14.6 Hz, COD-*C*H), 32.9 (COD-$CH_2$), 28.6 (COD-$CH_2$), 21.4 (Ar-$CH_3$), 20.0 (Ar-$CH_3$), 18.4 (Ar-$CH_3$). Anal. calcd for $C_{29}H_{36}BrN_2Rh$: C, 58.50; H, 6.09; N, 4.70. Found: C, 58.56; H, 6.13; N, 4.67. MS (ESI$^+$): *m/z* 515.1 [M − Br]$^+$, calcd 515.5.

*Complex* ***5a***

Yield: 0.506 g (81%). $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 6.85 (s, 4 H, C$H_{arom}$), 5.57 (d, *J* = 14.0 Hz, 2 H, Mes-C$H_2$-N-), 5.10 (d, *J* = 14.0 Hz, 2 H, Mes-C$H_2$-N-), 5.06 (br, 2 H, COD-C*H*), 3.67 (br, 2 H, COD-C*H*), 2.90 (s, 4 H, -N-C$H_2CH_2$-N-), 2.45–2.41 (m, 4 H, COD-C$H_2$), 2.42 (s, 12 H, Ar-C$H_3$), 2.25 (s, 6 H, Ar-C$H_3$), 2.00–1.94 (m, 4 H, COD-C$H_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 214.5 (d, $J_{Rh-Carbene}$ = 46.9 Hz, $C_{carbene}$), 138.5 (Ar-*C*), 137.8 (Ar-*C*), 129.5 (Ar-*C*), 129.2 (Ar-*C*), 99.2 (d, $J_{Rh-C}$ = 6.1 Hz, COD-*C*H), 68.0 (d, $J_{Rh-C}$ = 15.4 Hz, COD-*C*H), 48.9 (Mes-$CH_2$-N-), 47.5 (-N-$CH_2CH_2$-N-), 33.2 (COD-$CH_2$), 28.9 (COD-$CH_2$), 21.2 (Ar-$CH_3$), 20.9 (Ar-$CH_3$). Anal. Calcd for $C_{31}H_{42}BrN_2Rh$: C, 59.53; H, 6.77; N, 4.48. Found: C, 59.57; H, 6.81; N, 4.46. MS (ESI$^+$): *m/z* 545.3 [M − Br]$^+$, calcd 545.6.

*Complex* ***5b***

Yield: 0.545 g (87%). $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 6.89 (s, 4 H, C$H_{arom}$), 6.07 (s, 2 H, -N-C*HCH*-N-), 5.86 (d, *J* = 14.0 Hz, 2 H, Mes-C$H_2$-N-), 5.45 (d, *J* = 14.0 Hz, 2 H, Mes-C$H_2$-N-), 5.18 (br, 2 H, COD-C*H*), 3.65 (br, 2 H, COD-C*H*), 2.49–2.40 (m, 4 H, COD-C$H_2$), 2.29 (s, 12 H, Ar-C$H_3$), 2.28 (s, 6 H, Ar-C$H_3$), 2.03–1.95 (m, 4 H, COD-C$H_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 182.3 (d, $J_{Rh-Carbene}$ = 49.1 Hz, $C_{carbene}$), 138.7 (Ar-*C*), 138.6 (Ar-*C*),

129.6 (Ar-*C*), 128.4 (Ar-*C*), 118.4 (-N-*C*HC*H*-N-), 98.1 (d, $J_{Rh-C}$ = 6.9 Hz, COD-*C*H), 68.8 (d, $J_{Rh-C}$ = 14.6 Hz, COD-*C*H), 49.3 (Mes-*C*$H_2$-N-), 33.1 (COD-$CH_2$), 29.4 (COD-$CH_2$), 21.3 (Ar-$CH_3$), 20.4 (Ar-$CH_3$). Anal. Calcd for $C_{29}H_{36}BrN_2Rh$: C, 59.72; H, 6.47; N, 4.49. Found: C, 59.66; H, 6.42; N, 4.53. MS ($ESI^+$): *m/z* 543.5 $[M - Br]^+$, calcd 543.7.

*Complex* ***6a***

Yield: 0.538 g (88%). $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 6.95 (s, 1 H, C$H_{arom}$), 6.82 (s, 2 H, C$H_{arom}$), 6.80 (s, 1 H, C$H_{arom}$), 5.62 (d, *J* = 14.4 Hz, 1 H, Mes-C$H_2$-N-), 5.20 (d, *J* = 14.4 Hz, 1 H, Mes-C$H_2$-N-), 4.97–4.92 (m, 1 H, COD-C*H*), 4.77–4.72 (m, 1 H, COD-C*H*), 3.75–3.71 (m, 1 H, COD-C*H*), 3.55–3.41 (m, 2 H, -N-$CH_2CH_2$-N-), 3.20–3.01 (m, 3 H, COD-C*H* + -N-$CH_2CH_2$-N-), 2.57 (s, 3 H, Ar-$CH_3$), 2.36 (s, 6 H, Ar-$CH_3$), 2.34–2.28 (m, 1 H, COD-$CH_2$), 2.25 (s, 3 H, Ar-$CH_3$), 2.21 (s, 3 H, Ar-$CH_3$), 2.13–2.04 (m, 1 H, COD-$CH_2$), 1.94 (s, 3 H, Ar-$CH_3$), 1.89–1.75 (m, 2 H, COD-$CH_2$), 1.68–1.58 (m, 2 H, COD-$CH_2$), 1.45–1.38 (m, 2 H, COD-$CH_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 212.3 (d, $J_{Rh-Carbene}$ = 46.1 Hz, $C_{carbene}$), 138.5 (Ar-*C*), 138.3 (Ar-*C*), 138.0 (Ar-*C*), 137.7 (Ar-*C*), 136.8 (Ar-*C*), 135.5 (Ar-*C*), 130.0 (Ar-*C*), 129.7 (Ar-*C*), 129.5 (Ar-*C*), 128.6 (Ar-*C*), 97.5 (d, $J_{Rh-C}$ = 6.7 Hz, COD-*C*H), 97.2 (d, $J_{Rh-C}$ = 6.7 Hz, COD-*C*H), 69.5 (d, $J_{Rh-C}$ = 14.5 Hz, COD-*C*H), 67.8 (d, $J_{Rh-C}$ = 14.5 Hz, COD-*C*H), 51.2 (-N-$CH_2CH_2$-N-), 50.4 (Mes-$CH_2$-N-), 47.7 (-N-$CH_2CH_2$-N-), 33.8 (COD-$CH_2$), 31.9 (COD-$CH_2$), 29.2 (COD-$CH_2$), 28.5 (COD-$CH_2$), 21.2 (Ar-$CH_3$), 21.1 (Ar-$CH_3$), 20.7 (Ar-$CH_3$), 18.0 (Ar-$CH_3$). Anal. Calcd for $C_{30}H_{40}BrN_2Rh$: C, 58.93; H, 6.59; N, 4.58. Found: C, 58.86; H, 6.62; N, 4.57. MS ($ESI^+$): *m/z* 531.4 $[M - Br]^+$, calcd 531.6.

*Complex* ***6b***

Yield: 0.527 g (86%). $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.00 (s, 1 H, C$H_{arom}$), 6.86 (s, 2 H, C$H_{arom}$), 6.82 (s, 1 H, C$H_{arom}$), 6.55 (d, *J* = 2.0 Hz, 1 H, -N-C*H*CH-N-), 6.32 (s, 1 H, -N-CHC*H*-N-), 5.83 (s, 2 H, Mes-C$H_2$-N-), 4.98–4.94 (m, 1 H, COD-C*H*), 4.86–4.81 (m, 1 H, COD-C*H*), 3.59–3.55 (m, 1 H, COD-C*H*), 3.08–3.03 (m, 1 H, COD-C*H*), 2.42 (s, 3 H, Ar-$CH_3$), 2.39–2.21 (m, 2 H, COD-$CH_2$), 2.29 (s, 3 H, Ar-$CH_3$), 2.26 (s, 6 H, Ar-$CH_3$), 2.23 (s, 3 H, Ar-$CH_3$), 2.15–2.10 (m, 1 H, COD-$CH_2$), 1.98–1.92 (m, 1 H, COD-$CH_2$), 1.80–1.62 (m, 2 H, COD-$CH_2$), 1.48 1.37 (m, 2 H, COD-$CH_2$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 180.3 (d, $J_{Rh-Carbene}$ = 50.7 Hz, $C_{carbene}$), 137.6 (Ar-*C*), 137.4 (Ar-*C*), 137.3 (Ar-*C*), 136.1 (Ar-*C*), 135.3 (Ar-*C*), 133.5 (Ar-*C*), 128.6 (Ar-*C*), 128.4 (Ar-*C*), 127.8 (Ar-*C*), 127.0 (Ar-*C*), 121.6 (-N-*C*HCH-N-), 118.3 (-N-CHC*H*-N-), 95.6 (d, $J_{Rh-C}$ = 6.7 Hz, COD-*C*H), 95.4 (d, $J_{Rh-C}$ = 6.7 Hz, COD-*C*H), 67.5 (d, $J_{Rh-C}$ = 14.3 Hz, COD-*C*H), 67.3 (d, $J_{Rh-C}$ = 14.3 Hz, COD-*C*H), 49.9 (Mes-$CH_2$-N-), 33.0 (COD-$CH_2$), 30.4 (COD-$CH_2$), 28.4 (COD-$CH_2$), 27.3 (COD-$CH_2$), 20.1 (Ar-$CH_3$), 20.0 (Ar-$CH_3$), 19.5 (Ar-$CH_3$), 18.9 (Ar-$CH_3$), 16.6 (Ar-$CH_3$). Anal. Calcd for $C_{30}H_{38}BrN_2Rh$: C, 59.12; H, 6.28; N, 4.60. Found: C, 59.05; H, 6.23; N, 4.64. MS ($ESI^+$): *m/z* 529.2 $[M - Br]^+$, calcd 529.5.

### General Procedure for Preparation of the [(NHC)RhBr(CO)$_2$] Complexes

[(NHC)RhBr(cod)] (**4b–6b**) (0.2 mmol) was dissolved in $CH_2Cl_2$ (5 ml) and carbon monoxide was bubbled through the solution for 1 h. The color of the solution changed from orange to pale yellow. The solution was concentrated to ~2 ml and pentane was added. The pale-yellow solid that separated out was filtered and washed with pentane. The following complexes (**7b–9b**) were synthesized according to this procedure.

*Complex* ***7b***

Yield: 0.102 g (94%). IR ($CH_2Cl_2$): $\nu_{CO}$ = 2079.7, 1996.7 $cm^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.12 (s, 2 H, -N-C*H*C*H*-N-), 7.02 (s, 4 H, C$H_{arom}$), 2.37 (s, 6 H, Ar-$CH_3$), 2.23 (s, 12 H, Ar-$CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 185.3 (d, $J_{Rh-Carbene}$ = 54.5 Hz, $C_{carbene}$), 183.0 (d, $J_{Rh-C}$ = 74.3 Hz, *C*O), 177.6 (d, $J_{Rh-C}$ = 44.5 Hz, *C*O), 139.6 (Ar-*C*), 135.5 (Ar-*C*), 135.4 (Ar-*C*), 129.5 (Ar-*C*), 124.1 (-N-*C*HC*H*-N-), 21.4 (Ar-$CH_3$), 18.7 (Ar-$CH_3$). Anal. Calcd for $C_{23}H_{24}BrN_2O_2Rh$: C, 50.85; H, 4.45; N, 5.16. Found: C, 50.76; H, 4.42; N, 5.20.

*Complex* ***8b***

Yield: 0.104 g (91%). IR ($CH_2Cl_2$): $\nu_{CO}$ = 2078.9, 2000.3 $cm^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 6.92 (s, 4 H, C$H_{arom}$), 6.31 (s, 2 H, -N-C*H*C*H*-N-), 5.40 (s, 4 H, Mes-C$H_2$-N-), 2.30 (s, 6 H, Ar-$CH_3$), 2.27 (s, 12 H, Ar-$CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 186.5 (d, $J_{Rh-Carbene}$ = 53.7 Hz, $C_{carbene}$), 182.8 (d, $J_{Rh-C}$ = 76.0 Hz, *C*O), 173.4 (d, $J_{Rh-C}$ = 43.0 Hz, *C*O), 139.0 (Ar-*C*), 138.4 (Ar-*C*), 129.8 (Ar-*C*), 128.1 (Ar-*C*), 119.8 (-N-*C*HC*H*-N-), 50.1 (Mes-$CH_2$-N-), 21.2 (Ar-$CH_3$), 20.3 (Ar-$CH_3$). Anal. Calcd for $C_{25}H_{28}BrN_2O_2Rh$: C, 52.56; H, 4.94; N, 4.90. Found: C, 52.64; H, 5.01; N, 4.93.

*complex* ***9b***

Yield: 0.108 g (97%). IR ($CH_2Cl_2$): $\nu_{CO}$ = 2078.5, 2000.1 $cm^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 6.99 (s, 2 H, C$H_{arom}$), 6.95 (s, 2 H, C$H_{arom}$), 6.83 (d, *J* = 2.0 Hz, 1 H, -N-C*H*CH-N-), 6.63 (d, *J* = 2.0 Hz, 1 H, -N-CHC*H*-N-), 5.58 (s, 2 H, Mes-C$H_2$-N-), 2.37 (s, 3 H, Ar-$CH_3$), 2.34 (s, 6 H, Ar-$CH_3$), 2.32 (s, 3 H, Ar-$CH_3$), 2.11 (s, 6 H, Ar-$CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 186.1 (d, $J_{Rh-Carbene}$ = 52.9 Hz, $C_{carbene}$), 182.6 (d, $J_{Rh-C}$ = 76.0 Hz, *C*O), 175.2 (d, $J_{Rh-C}$ = 43.0 Hz, *C*O), 139.6 (Ar-*C*), 138.9 (Ar-*C*), 138.3 (Ar-*C*), 135.6 (Ar-*C*), 135.4 (Ar-*C*), 129.8 (Ar-*C*), 129.5 (Ar-*C*), 128.6 (Ar-*C*), 123.4 (-N-*C*HC*H*-N-), 120.8 (-N-C*H*C*H*-N-), 50.9 (Mes-$CH_2$-N-), 21.4 (Ar-$CH_3$), 21.3 (Ar-$CH_3$), 20.3 (Ar-$CH_3$), 18.7 (Ar-$CH_3$). Anal. calcd for $C_{24}H_{26}BrN_2O_2Rh$: C, 51.73; H, 4.70; N, 5.03. Found: C, 51.67; H, 4.73; N, 4.98.

### General Procedure for the Transfer Hydrogenation Reaction

The tested complex (0.02 mmol; 0.5 mol%) was dissolved in a solution of KOH (0.2 mmol) and 2-propanol (20 ml) in a two-necked flask. The solution was heated to 82 °C for 30 min. Subsequently, acetophenone (4 mmol) was added. After the desired reaction time the solution was allowed to cool and quenched with 1 M HCl, extracted with $CH_2Cl_2$ and the organic phase separated. The reaction progress was monitored by $^1$H NMR and the results for each experiment are averages over two runs.

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