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RHODIUM(I) N-HETEROCYCLIC CARBENE COMPLEXES AS CATALYSTS FOR THE ANTI-MARKOVNIKOV HYDROAMINATIONS OF STYRENE

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Abstract – A series of new rhodium(I) complexes with benzimidazole based N-heterocyclic carbene (NHC) ligand were synthesized by reactions of benzimidazolium salts with $[Rh(OMe)COD]_2$. The characterization of rhodium(I) complexes with the general formula [RhCl(NHC)(η^4-1,5-cyclooctadiene)] was done by physicochemical and spectroscopic methods. All the synthesized complexes were tested as catalysts in the intermolecular hydroamination reactions between styrene with aromatic amines in ionic liquid. All of these complexes tested here are catalytically active for the intermolecular hydroamination of styrene with aromatic amines in ionic liquid. The anti-Markovnikov addition products were obtained selectively by using 1 mol% of the rhodium complex.

INTRODUCTION

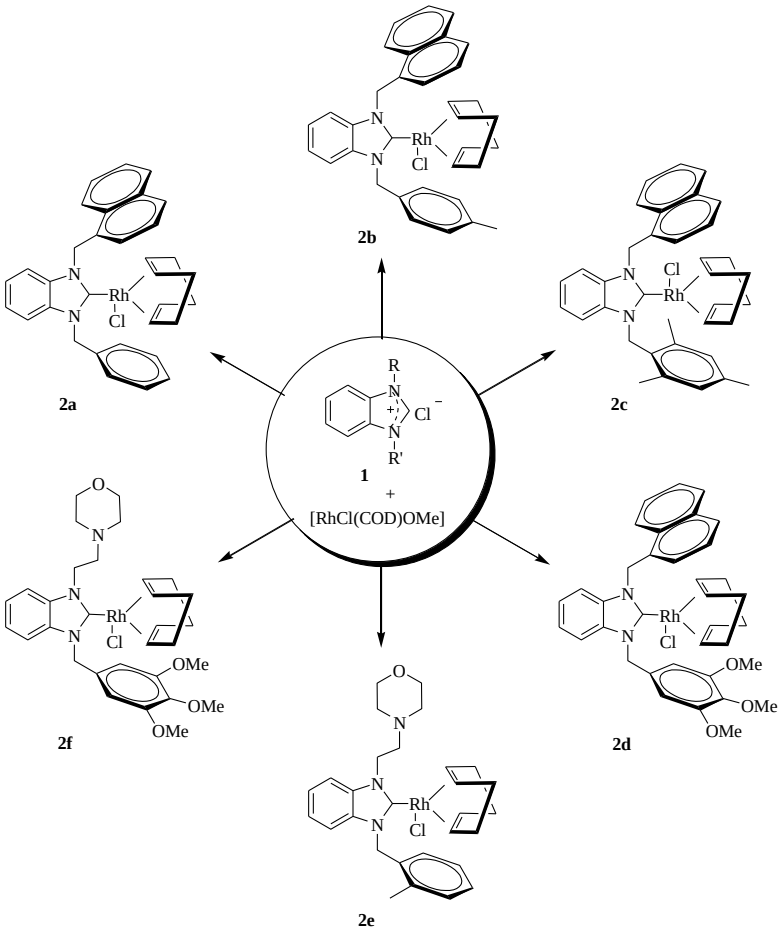
The addition of the N-H bonds to alkenes or alkynes termed as hydroamination is one of the most efficient ways of accessing nitrogen-containing compounds, which are important organic chemical materials and precursors widely used in pharmaceuticals, agrochemicals, and various bulk and fine chemicals.[1-5] Therefore, a great effort has been devoted toward the synthesis and derivatization of amine-functionalized molecules.[6] Hydroamination of carbon-carbon multiple bonds is an efficient atom-economic reaction which meets most of the principles of green chemistry for the synthesis of amine derivatives.

Hydroamination reactions may be inter- or intramolecularly, which following Markovnikov or anti-Markovnikov regioselectivity.[7-9] Particularly, intramolecular hydroamination of aminoalkenes or aminoalkynes provide a useful method for the construction of nitrogen-containing heterocycles that are prevalent in natural products and biologically active compounds.[10-19] The hydroamination reaction is thermodynamically feasible under normal conditions, but there is a high activation energy barrier due to electrostatic repulsions between the lone pair of the nitrogen atom and the π-bond of electron-rich alkene.[20-22] To overcome this thermodynamic limitation, a wide variety of metal-based catalysts, including complexes of main group metals, lanthanides, and both early and late transition metals have been developed for the hydroamination reactions.[23-26] Also, Lewis and Brønsted acids have been used for this transformation.[27-40] In addition, several asymmetric versions of this reaction have performed using chiral catalysts for the preparation of enantiopure amines, which are key intermediates for the organic compounds in fine chemicals and pharmaceutial industry.[41-44] Catalytic hydroamination of alkenes and alkynes have been intensively studied, where the addition of amine to double bond of alkene via either inter- or intramolecularly produces secondary amine, the addition of amine is regioselective, and it usually follows the Markovnikov rule.[45-50] On the other hand, only several catalytic systems with transition metal complex catalysts have been developed for the hydroamination providing anti-Markovnikov products.[51-57] Especially, anti-Markovnikov products have been obtained generally, when rhodium and ruthenium complexes are used as catalyst.[58-63] For example, in 2003, Hartwig reported the anti-Markovnikov hydroamination of vinyl(hetero)arenes with dialkylamines using Rh/DPEphos catalysis, yielding phenethylamine products in good yields.[60] The following year, Hartwig further detailed the anti-Markovnikov hydroamination of vinylarenes with cyclic amines utilizing combinations of ruthenium complexes and phosphine ligands in presence of Brønsted acid.[61] Recently, ionic liquids (ILs) have attracted much attention due to their unique properties and applications in the diverse areas. They are an important class of organic salts that are usually liquid at room temperature. ILs posses many valuable properties such as chemical and thermal stability, structure and property tunabilities, negligible vapor pressure, non-flammability, good dissolving ability and recyclability. Their unique properties make them good solvents for a broad spectrum of inorganic, organic and polymeric materials. Reactions performed in ionic liquids as solvent often show rate enhancement, selectivity and higher yields with respect to traditional solvents.[64,65] However, there are a few reports related to the use of ionic liquids as solvent in hydroamination reactions.[66-68] We have previously reported the synthesis of $PdCl_2(NHC)_2$ and NHC-palladium(II)-PEPPSI complexes and their catalytic activities in the intermolecular hydroamination reactions.[69-71] A variety of NHC complexes have been widely used as catalysts in hydroamination reactions.[72-79] However, the use of rhodium(I)-NHC complexes is rare.[80,81] Therefore, we now report the synthesis of rhodium(I)-NHC complexes and their use as effective catalysts in hydroamination of styrene.

RESULTS AND DISCUSSION

Synthesis of rhodium complexes

A number of methodologies have been developed to synthesize the N-heterocyclic carbene rhodium (COD) complexes include (i) reaction of a free carbene with dimeric precursor $[Rh(COD)Cl_2]_2$, (ii) in situ deprotonation of azolium salts with a rhodium dimer $[Rh(OMe)COD]_2$, (iii) reaction of a electron-rich enetetramines with $[Rh(COD)Cl_2]_2$ under C=C bond cleavage, (iv) transfer of the carbene unit from silver(I)-NHC complex to rhodium metal.[82-85] Among them, we used the second preparation pathway for the synthesis of Rh(I)-NHC complexes. The advantage of this route is that no pregeneration of the free carbene is necessary and the methoxy ligands are protonated to give methanol upon reaction with the benzimidazolium salt. The reaction of rhodium dimer $[Rh(OMe)COD]_2$ with two equivalents of 1,3-dialkylbenzimidazolium chloride salts in tetrahydrofuran under reflux gave the corresponding (COD)-rhodium(I)-NHC complexes **2a-f** (Scheme 1).



Scheme 1. The synthesis of rhodium(I)-NHC complexes

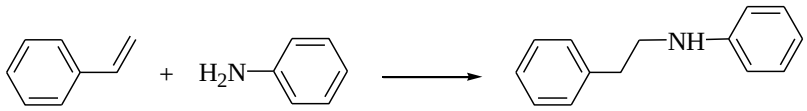
After purification, rhodium complexes were isolated as yellow-orange crystalline solids in good yields of 75-89%. These complexes are very stable against air and moisture in the solid-state. The structures of

rhodium complexes were determined by NMR spectroscopy and elemental analysis, which support the proposed structures. NMR analyses of the complexes **2a-f** show that the N-heterocyclic carbene ligand have coordinated to rhodium. The formation of Rh(I)-NHC complexes **2a-f** were confirmed by the disappearance of the resonance signals of benzimidazolium C2-proton and C2-carbon in NMR spectra. Rhodium(I)-NHC complexes exhibit characteristic ^{13}C NMR chemical shifts, which provide a useful diagnostic tool for this type of metal carbene complexes. The chemical shifts of the carbene carbon of rhodium complexes were observed as a doublet between 196.9 and 198.4 ppm for **2a-f** and coupling constants $J(^{103}Rh\text{-}^{13}C)$ were 50.6 and 51.3 Hz, and these values were similar to those found for other rhodium(I) carbene complexes.[86] The elemental analysis data of the complexes **3a-f** are in agreement with the proposed formulas.

Catalytic studies

The hydroamination of alkenes using anilines is a convenient method for the synthesis of alkylanilines, which play a key role in crop protection and pharmaceutical industries, and a number of transition metal complexes have been used for this reaction. The catalytic activities of new rhodium complexes **2a-f** for the intermolecular hydroamination of styrene using aromatic amines were evaluated. Initially, the reaction of styrene with aniline was selected as a model reaction to determine the optimal catalytic conditions with **2a** as a catalyst. The effect of the base and solvent were examined. The results are summarized in Table 1. Triethylamine, KOH, and *t*-BuOK were tested as the base. Among them, *t*-BuOK displayed the highest reactivity (Table 1, entry 8). KOH was less effective (Table 1, entry 7). It is noteworthy that, in the absence of rhodium complex, only 7% yield was observed (Table 1, entry 9). The choice of solvent is usually important in achieving an efficient hydroamination reaction. As a solvent, dimethoxyethane, toluene, dioxane and *N*-butylpyridinium hexafluorophosphate (IL) were used for the intermolecular hydroamination of styrene with aniline. High yield was obtained with *N*-butylpyridinium hexafluorophosphate (Table 1, entry 8). The imidazolium based ionic liquids which contain acidic hydrogen are readily converted to N-heterocyclic carbenes by use of the strong bases. Therefore, the *N*-butylpyridinium hexafluorophosphate was used as ionic liquid in this study. The catalytic reactions were carried out using 1 mol% of **2a-f**, 1.10 mmol *t*-BuOK, 1.10 mmol styrene and 1.00 mmol aniline in 1 mL *N*-butylpyridinium hexafluorophosphate at 160 or 185 ^{o}C for 1 or 2 h. Under these reaction conditions, the rhodium-catalyzed hydroamination of styrene with aromatic amines (aniline, 4-chloroaniline, 4-methoxyaniline and 2-aminopyridine) to prepare diverse phenethylamines were examined. All substrates gave complete anti-Markovnikov regioselectivity, and in all cases, only the anti-Markovnikov products were formed. The chemical characterizations of the products were made by NMR. The conversions were screened by GC analysis and results were presented in Table 2.

Table 1. Screening of intermolecular hydroamination reaction conditions[a]

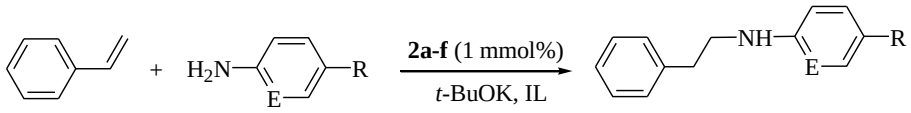


Entry	Cat.	Solvent	Base	Yield (%)
1	**2a**	DME	NEt_3	15
2	**2a**	DME	KOH	43
3	**2a**	DME	*t*-BuOK	47
4	**2a**	toluene	*t*-BuOK	26
5	**2a**	dioxane	*t*-BuOK	29
6	**2a**	IL	NEt_3	41
7	**2a**	IL	KOH	61
8	**2a**	IL	*t*-BuOK	79
9	**-**	IL	*t*-BuOK	7

[a]Reaction conditions: **2a** (0.01 mmol), styrene (1.10 mmol), aniline (1.00 mmol), 160 ^{o}C, 1 h.

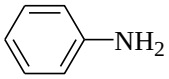
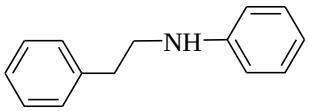
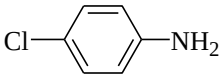
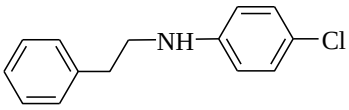
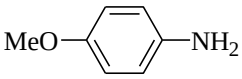
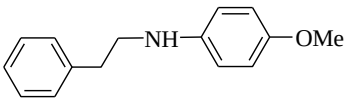
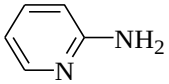
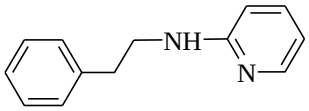
With the determined optimal conditions in hand, initially, the reaction of styrene (**3**) with aniline (**4**) was investigated in the presence of complexes **2a-f** as catalysts. In all reactions, only the anti-Markovnikov hydroamination product, *N*-(2-phenylethyl)aniline (**8**) was obtained selectively in high yields for all six catalysts (Table 2, entries 1-6). The best yields were achieved with catalysts **2b** and **2f**. The formation of Markovnikov, N-dialkylation or C-alkylation products were not detected in these reactions. Then, *p*-chloroaniline (**5**), *p*-methoxyaniline (**6**) and 2-aminopyridine (**7**) were reacted with styrene in the presence of complexes **2a-f** under the same reaction conditions (Table 2, entries 7-24). The treatment of styrene with *p*-chloroaniline (**5**) (Table 2, entries 7-12) gave *N*-(2-phenylethyl)-4-chloroaniline with anti-Markovnikov selectivity in high yields under same conditions. However, the reaction of styrene with *p*-methoxyaniline (**6**) and 2-aminopyridine (**7**) gave slightly lower yield of the corresponding secondary amines (**10** and **11**) (Table 2, entries 13-24). We finally examined the reactions of *p*-chloroaniline with *p*-substituted styrenes in the presence of complexes **2f** as catalyst under the same reaction conditions. The reaction of *p*-chloroaniline with *p*-methylstyrene, *p*-methoxystyrene and *p*-fluorostyrene also afforded corresponding anti-Markovnikov addition products in 89%, 85% and 94% yields, respectively. These results clearly show that the electron-donating substituent (*p*-methoxy) on aniline gave slightly lower yield when compared that of aniline. Among the tested complexes, rhodium complex (**2f**) with methoxy substituted benzyl and morpholinoethyl groups exhibited higher catalytic activities compared to the other five complexes for anti-Markovnikov hydroamination reactions of styrene with aromatic amines.

Table 2. Hydroamination of styrene using aromatic amines by **2a-f**[a-c]



3 **4-7** **8-11**

E : CH or N

Entry	Ar-NH_2	Catalyst	Product	Yield (%)
1		**2a**		79
2		**2b**		95
3		**2c**		91
4		**2d**		83
5	**4**	**2e**	**8**	90
6		**2f**		96
7		**2a**		81
8		**2b**		96
9		**2c**		88
10		**2d**		86
11	**5**	**2e**	**9**	92
12		**2f**		98
13		**2a**		74
14		**2b**		82
15		**2c**		85
16		**2d**		71
17	**6**	**2e**	**10**	79
18		**2f**		87
19		**2a**		64[d]
20		**2b**		65[d]
21		**2c**		58[d]
22		**2d**		65[d]
23	**7**	**2e**	**11**	56[d]
24		**2f**		66[d]

[a]Reaction conditions: **2a-f** (0.01 mmol), styrene (1.10 mmol), aromatic amine (1.00 mmol), *t*-BuOK (1.10 mmol), *N*-butylpyridinium hexafluorophosphate (1 mL). [b]Yields were determined GC, dodecane was used as internal standard, products were characterized by NMR. [c]160 °C, 1 h. [d]185 °C, 2 h.

CONCLUSION

In summary, rhodium(I)-NHC complexes **2a-f** have been readily prepared by reaction of benzimidazolium salts with $[Rh(OMe)COD]_2$ in tetrahydrofuran and characterized by elemental analysis and spectroscopic methods. The catalytic activity of these complexes was investigated in the intermolecular hydroamination reaction of styrene with aromatic amines in ionic liquid. These complexes catalyzed the hydroamination of styrene with aniline, *p*-chloroaniline, 2-aminopyridine and *p*-methoxyaniline with very high anti-Markovnikov selectivity. The hydroamination reactions proceeded in good to excellent yield with regioselectivity and in all cases, only the anti-Markovnikov addition products were obtained. No formation of the Markovnikov or hydroarylation products were observed.

EXPERIMENTAL

All preparative reactions for the rhodium(I)-NHC complexes (**2a-f**) were carried out under argon in flame-dried glassware using standard Schlenk techniques. The solvents were purified by distillation over the drying agents indicated, and transferred under Ar; THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). All reagents were purchased from Sigma-Aldrich, Merck or Fluka. Benzimidazolium salts (**1**) were prepared according to procedures described in the literature.[70] All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker AC300P FT spectrometer operating at 300.13 (^1H) or 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hertz. Gas chromatography was carried out by GC-FID on an Agilent 6890N gas chromatograph equipped with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. Elemental analyses were obtained with a LECO CHNS-932 elemental analyzer.

Synthesis of benzimidazolium salts 1

To a solution of 1-alkylbenzimidazole (1.69 g, 6.55 mmol) in DMF (5 mL), alkyl halides (6.55 mmol) was added. The reaction mixture was stirred at room temperature for 2 h and heated at 50 °C for 18 h. After reaction completed, the reaction mixture was cooled to room temperature. Et_2O (10 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with Et_2O and dried under vacuum. The crude product was recrystallized from $EtOH/Et_2O$.

Synthesis of rhodium(I)-NHC complexes 2

To a solution of 1,3-dialkylbenzimidazolium chloride (0.40 mmol) in THF (10 mL) was added rhodium dimer $[Rh(OMe)COD]_2$ (0.20 mmol) and the resulting mixture was stirred at reflux for 12 h. After

removal of the solvent, the residue was washed with Et_2O (10 mL) and dried under vacuum. The crude product was recrystallized from CH_2Cl_2/Et_2O, and yellow-orange crystals were obtained.

Chloro(η^4-1,5-cyclooctadiene)[1-benzyl-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]-rhodium(I) 2a

Yield: 79%, mp 189-190 °C. ^{1}H NMR ($CDCl_3$) δ: 1.29-2.51 (m, 8H, C*H*$_{2COD}$), 3.49 and 6.31 (m, 4H, C*H*$_{COD}$), 5.15 (s, 2H, C*H*$_2$C$_6$H$_5$), 6.27 (s, 2H, C*H*$_2$C$_{10}$H$_7$), 6.34-8.44 (m, 16H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 28.5, 28.7, 32.4 and 32.9 (*C*H$_{2COD}$), 50.1 (*C*H$_2$C$_6$H$_5$), 53.1 (*C*H$_2$C$_{10}$H$_7$), 69.2, 100.3 and 100.7 (d, J_{Rh-C} = 6.1 Hz and J_{Rh-C} = 14.3 Hz, *C*H$_{COD}$), 110.8, 111.1, 122.6, 122.7, 122.8, 123.5, 125.4, 126.3, 126.9, 127.1, 127.9, 128.2, 128.9, 129.0, 130.6, 131.8, 134.9, 135.5 and 136.2 (Ar-*C*), 198.4 (d, $J_{Rh-Carbene}$ = 51.3 Hz, Rh-*C*$_{carbene}$). Anal. Calcd for $C_{33}H_{32}N_2ClRh$: C, 66.62; H, 5.42; N, 4.71. Found: C, 66.61; H, 5.40; N, 4.71.

Chloro(η^4-1,5-cyclooctadiene)[1-(4-methylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]rhodium(I) 2b

Yield: 89%, mp 236-237 °C. ^{1}H NMR ($CDCl_3$) δ: 1.60-2.34 (m, 4H, C*H*$_{2COD}$), 2.37 (s, 3H, CH$_2$C$_6$H$_4$C*H*$_3$-4), 3.32 and 3.41 (m, 4H, C*H*$_{2COD}$), 5.13 (s, 2H, C*H*$_2$C$_6$H$_4$CH$_3$-4), 6.28 (s 2H, C*H*$_2$C$_{10}$H$_7$), 6.15-6.38 (m, 4H, C*H*$_{COD}$), 6.92-8.46 (m, 15H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 21.21 (CH$_2$C$_6$H$_4$*C*H$_3$-4), 28.5 and 32.7 (*C*H$_{2COD}$), 50.1 (*C*H$_2$C$_6$H$_4$CH$_3$-2), 52.9 (*C*H$_2$C$_{10}$H$_7$), 69.2, 100.2 and 100.6 (d, J_{Rh-C} = 6.8 Hz and J_{Rh-C} = 14.3 Hz, *C*H$_{COD}$), 110.7, 110.9, 122.2, 122.5, 122.8, 123.3, 123.5, 125.4, 126.2, 126.3, 126.8, 126.9, 128.1, 128.2, 128.4,128.9, 129.0, 129.7, 130.5, 130.6 131.8, 131.9, 133.7, 135.2, 135.3, 135.4, 138.4 and 138.5 (Ar-*C*), 198.1 (d, $J_{Rh-Carbene}$ = 51.5 Hz, Rh-*C*$_{carbene}$). Anal. Calcd for $C_{34}H_{34}N_2ClRh$: C, 67.05; H, 5.63; N, 4.60. Found: C, 67.03; H, 5.66; N, 4.58.

Chloro(η^4-1,5-cyclooctadiene)[1-(2,4,6-trimethylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]rhodium(I) 2c

Yield: 85%, mp 254-256 °C. ^{1}H NMR ($CDCl_3$) δ: 1.69 and 2.26 (m, 6H, C*H*$_{2COD}$), 2.37 and 2.40 (s, 9H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$-2,4,6), 3.34-3.41 (m, 2H, C*H*$_{2COD}$), 5.11 (m, 4H, C*H*$_{COD}$), 6.07 and 6.28 (d, J = 15 Hz, 2H, C*H*$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 6.31 and 6.36 (s, 2H, C*H*$_2$C$_{10}$H$_7$), 6.45 and 6.48 (s, 2H, CH$_2$C$_6$*H*$_2$(CH$_3$)$_3$-2,4,6), 6.98-8.46 (m, 11H, NC$_6$*H*$_4$N and CH$_2$C$_{10}$*H*$_7$). ^{13}C NMR ($CDCl_3$) δ: 20.9 and 21.1 (CH$_2$C$_6$H$_2$(*C*H$_3$)$_3$-2,4,6), 28.1, 28.3, 32.5 and 32.8 (*C*H$_{2COD}$), 49.7 and 50.4 (*C*H$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 53.4 (*C*H$_2$C$_{10}$H$_7$), 68.3, 69.3, 69.8, 99.7, 100.2 and 100.4 (d, J_{Rh-C} = 6.8 Hz and J_{Rh-C} = 14.3 Hz, *C*H$_{COD}$), 113.7, 113.9, 122.6, 125.1, 125.2, 126.5, 126.9, 127.0, 127.1, 127.6, 128.1, 129.1, 130.1, 130.2, 130.6,

131.4, 131.7, 133.8, 137.9 and 139.6 (Ar-*C*), 197.5 (d, $J_{Rh\text{-}Carbene}$ = 51.5 Hz, Rh-$C_{carbene}$). Anal. Calcd for $C_{36}H_{38}N_2ClRh$: C, 67.87; H, 6.01; N: 4.40. Found: C, 67.85; H, 6.00; N, 4.41.

Chloro(η⁴-1,5-cyclooctadiene)[1-(3,4,5-trimethoxybenzyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]rhodium(I) 2d

Yield: 80%, mp 220-221 ºC. ^{1}H NMR ($CDCl_3$) δ: 2.38 (m, 2H, CH_{2COD}), 1.63-2.12(m, 6H, CH_{2COD}), 3.86 and 3.88 (s, 9H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 5.14 (m, 4H, CH_{COD}), 5.67 and 5.72 (s, 2H, C$H_2C_6H_2(OCH_3)_3$-3,4,5), 6.34 and 6.39 (s, 2H, C$H_2C_{10}H_7$), 6.72 and 6.77 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 6.94-8.45 (m, 11H, NC_6H_4N and $CH_2C_{10}H_7$). ^{13}C NMR ($CDCl_3$) δ: 28.5, 28.6, 32.3 and 33.1 (CH_{2COD}), 56.6 and 60.9 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 50.1 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 53.5 ($CH_2C_{10}H_7$), 69.2, 100.2 and 101.0 (d, $J_{Rh\text{-}C}$ = 6.8 Hz and $J_{Rh\text{-}C}$ = 14.3 Hz, CH_{COD}), 105.0, 110.6, 111.1, 122.6, 122.7, 122.8, 123.6, 125.3, 126.3, 126.9, 128.2, 129.0, 130.6, 131.5, 131.8, 133.7, 134.6, 135.5, 137.6 and 153.6 (Ar-*C*), 198.1 (d, $J_{Rh\text{-}Carbene}$ = 50.6 Hz, Rh-$C_{carbene}$). Anal. Calcd for $C_{36}H_{38}N_2ClO_3Rh$: C, 63.12; H, 5.59; N, 4.09. Found: C, 63.13; H, 5.60; N, 4.09.

Chloro(η⁴-1,5-cyclooctadiene)[1-(2-methylbenzyl)-3-(2-morpholinoethyl)benzimidazol-2-ylidene]-rhodium(I) 2e

Yield: 75%, mp 158-159 ºC. ^{1}H NMR ($CDCl_3$) δ: 1.88 (m, 4H, CH_{2COD}), 2.29 (m, 2H, CH_{2COD}), 2.52 (s, 3H $CH_2C_6H_4CH_3$-2), 2.68 (m, 4H, NCH_2CH_2O), 3.71 (t, *J* = 4.8 Hz, 4H, NCH_2CH_2O), 2.92, 3.14, 3.31 and 4.79 (m, 4H, NCH_2CH_2N), 5.03 (m, 4H, CH_{COD}), 5.65 and 6.55 (d, *J* = 1.4 Hz, 2H, C$H_2C_6H_4CH_3$-2), 6.47-7.35 (m, 8H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 19.8 ($CH_2C_6H_4CH_3$-2), 29.1, 29.7, 32.6 and 32.9 (CH_{2COD}), 46.1, 53.5, 54.1 and 57.5 ($NCH_2CH_2NCH_2CH_2O$), 67.1 ($CH_2C_6H_4CH_3$-2), 68.5, 69.4, 100.1 and 100.2 (d, $J_{Rh\text{-}C}$ = 3.2 Hz and $J_{Rh\text{-}C}$ = 14.3 Hz, CH_{COD}), 110.0, 110.8, 122.5, 122.6, 125.6, 126.3, 127.4, 130.5, 134.3, 134.9 and 135.0 (Ar-*C*), 197.5 (d, $J_{Rh\text{-}Carbene}$ = 51.5 Hz, Rh-$C_{carbene}$). Anal. Calcd for $C_{28}H_{35}N_3ClORh$: C, 59.21; H, 6.21; N, 7.40. Found: C, 59.24; H, 6.22; N, 7.39.

Chloro(η⁴-1,5-cyclooctadiene)[1-(3,4,5-trimethoxybenzyl)-3-(2-morpholinoethyl)benzimidazol-2-ylidene]rhodium(I) 2f

Yield: 77%, mp 123-124 ºC. ^{1}H NMR ($CDCl_3$) δ: 2.01(m, 4H, CH_{2COD}), 3.00 (m, 4H, CH_{2COD}), 3.82, 3.83 and 3.84 (s, 9H $CH_2C_6H_2(OCH_3)_3$-3,4,5), 2.70 (m, 4H, NCH_2CH_2O), 3.77 (t, *J* = 4.5 Hz, 4H, NCH_2CH_2O), 2.40, 3.21, 3.38 and 4.92 (m, 4H, NCH_2CH_2N), 5.20 (m, 4H, CH_{COD}), 5.64 and 6.55 (d, *J* = 1.5 Hz, 2H, C$H_2C_6H_2(OCH_3)_3$-3,4,5), 6.67 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 6.90-7.67 (m, 4H, NC_6H_4N). ^{13}C NMR ($CDCl_3$) δ: 28.4, 29.3, 32.6 and 33.3 (CH_{2COD}), 65.9 and 66.4 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 46.1,

53.4, 54.0, 56.6, 57.5 and 60.8 (NCH$_2$CH$_2$NCH$_2$CH$_2$O), 67.0 (CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-3,4,5), 68.5, 69.4, 100.2 and 100.7 (d, J_{Rh-C} = 6.8 Hz and J_{Rh-C} = 14.3 Hz, CH$_{COD}$), 104.9, 106.3, 110.0, 111.1, 122.5, 131.5, 134.5, 135.2, 137.6 and 153.6 (Ar-*C*), 196.9 (d, $J_{Rh-Carbene}$ = 50.6 Hz, *C*-Rh). Anal. Calcd for $C_{30}H_{39}N_3ClO_4Rh$: C, 55.95; H, 6.10; N, 6.52. Found: C, 55.92; H, 6.09; N, 6.55.

General procedure for the hydroamination of styrene

The Rh-NHC complexes **2** (1.0 mol%), *t*-BuOK (1.10 mmol), styrene (1.10 mmol), aromatic amine (1.00 mmol) and *N*-butylpyridinium hexafluorophosphate (1 mL) were added to a small Schlenk tube and the mixture was heated at 160-185 ^oC for 1 or 2 h. At the end of reaction, the mixture was cooled to room temperature, and water (5 mL) was added. The mixture was extracted with EtOAc. The organic phase was dried over anhydrous Na_2SO_4 and filtered through a short silica column. The filtrate was concentrated under reduced pressure, and purified by flash chromatography on silica gel (EtOAc/hexane; 1/5). The yields were calculated by GC analysis based on aromatic amines.

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