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RUTHENIUM(II) COMPLEXES WITH CHELATING N-HETEROCYCLIC CARBENES AND A RUTHENATE(II) COMPLEX AS CATALYSTS FOR THE ANTI-MARKOVNIKOV HYDROAMINATIONS OF STYRENE

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Abstract – New ruthenium chelate and ruthenate complexes were synthesized through the reaction of benzimidazolium salts and $[\text{RuCl}_2(p\text{-cymene})]_2$ in toluene and characterized by elemental analysis, ^1H NMR and ^{13}C NMR spectroscopy. These ruthenium complexes were tested as catalysts in the intermolecular hydroamination reactions between styrene with aromatic amines in ionic liquid. All of these complexes tested here showed good catalytic activity in these reactions. The hydroamination reactions regioselectively produced anti-Markovnikov addition products in moderate to good yields by using 1 mol% of the ruthenium complex.

INTRODUCTION

N-Heterocyclic carbenes (NHCs) are neutral, carbon-donor ligands, which have strong σ -donating and weak π -accepting ability.¹ The first use of N-heterocyclic carbenes as ligands for transition metals were independently reported by Öfele² and Wanzlick in 1968.³ Metal complexes of NHC ligands were extensively studied in 1970s by Lappert and co-workers.⁴ In 1991, Arduengo and co-workers successfully isolated and characterized the first stable free N-heterocyclic carbene.⁵ Since then, different types of NHCs, such as imidazolin-2-ylidenes, benzimidazolin-2-ylidenes, imidazolidin-2-ylidenes and

1,2,4-triazolin-5-ylidenes have been successfully synthesized and used as ligands in organometallic chemistry and catalysis.⁶⁻¹¹ Ruthenium complexes of these NHC ligands have been used as precatalysts in diverse organic transformations such as olefin metathesis, C-H bond activation, amine alkylation and transfer hydrogenation reactions.¹²⁻¹⁵ Also, ruthenium NHC complexes have been employed in medicinal applications and materials chemistry.^{16,17} Chelating NHCs including symmetrical bis-NHCs, NHCs with a secondary N-, O-, P- or S-donor group(s) on N-side arm and NHC-based pincer ligands are well-known structural motifs and have been used for the synthesis of various efficient catalysts in diverse transformations.¹⁸⁻²³ The ruthenium complexes with a chelating arene carbene ligand were first developed by Çetinkaya *et al.* in 2001.²⁴ They isolated the ruthenium complexes with a chelating arene carbene ligand by intramolecular displacement of *p*-cymene ligand with an aryl group on nitrogen atom of N-heterocyclic carbene ligand from reactions of enetetramines and $[\text{RuCl}_2(\textit{p}\text{-cymene})]_2$ in refluxing toluene. Similar complexes were obtained by heating of NHC-Ru(II)Cl₂(*p*-cymene) complexes in refluxing xylenes and by the reaction of imidazolium or benzimidazolium salts with $[\text{RuCl}_2(\textit{p}\text{-cymene})]_2$ in presence of Cs₂CO₃ in refluxing toluene by Çetinkaya group.²⁵ Also, they reported that this type of ruthenium complexes could not be obtained by the carbene transfer method.²⁶ They showed that this type of ruthenium-NHC complexes were effective as catalysts for alkene metathesis, cycloisomerisation, N-alkylation, ring-opening metathesis polymerization of norbornene, arylation, and transfer hydrogenation reactions.^{24, 26-29}

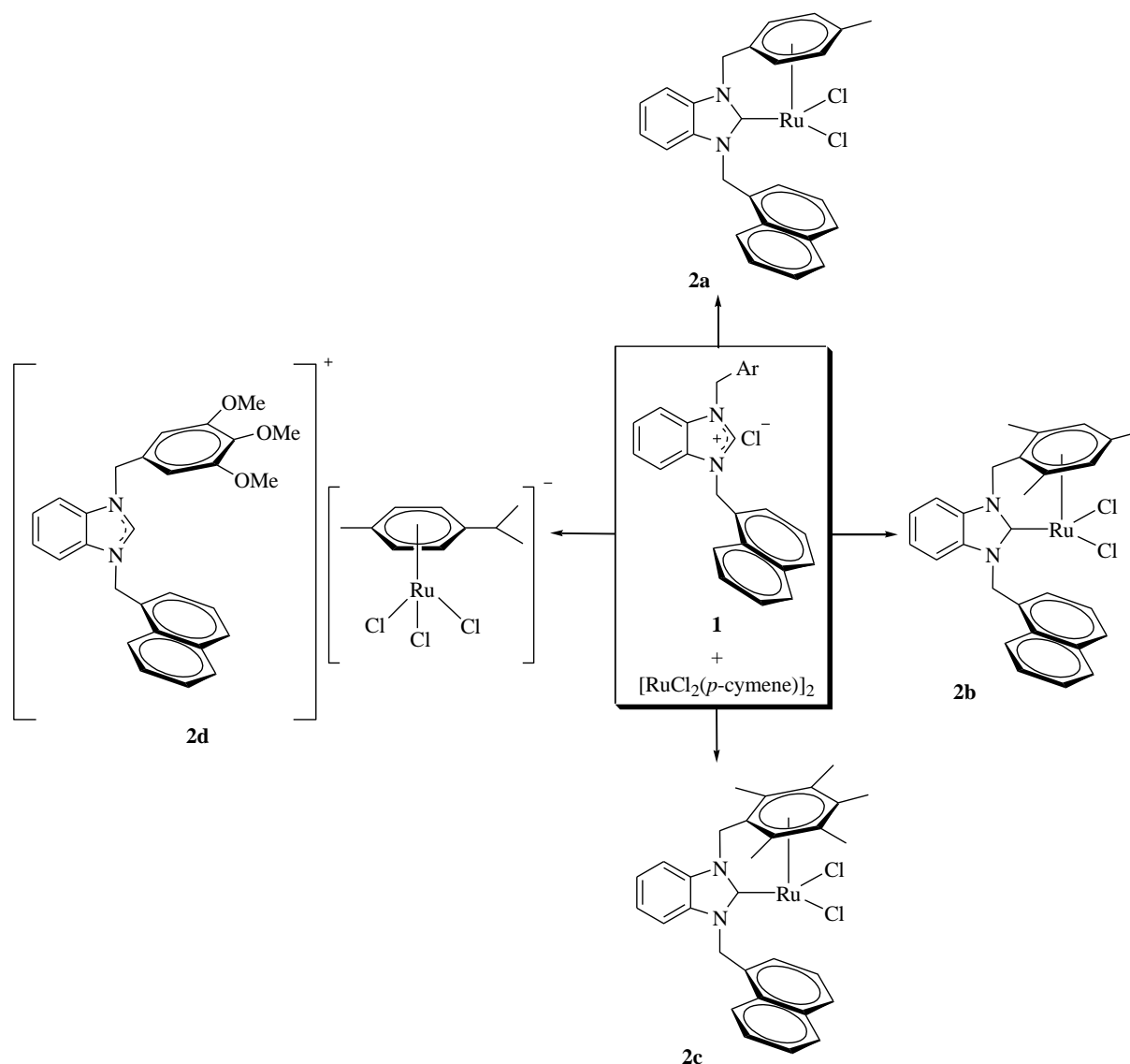
Hydroamination, the addition of the N-H bonds to alkenes or alkynes provides one of the most efficient methods for the preparation of amines or chiral amines, which are important building blocks for the synthesis of biologically active compounds, and various bulk and fine chemicals.³⁰⁻³⁴ Hydroamination reactions have received intensive attention because of 100% atom efficiency, broad availability and low-cost starting materials. Due to the thermodynamic characteristics of hydroamination reactions, this transformation required use of the catalytic systems. To date, a wide variety of metal-based catalysts, including complexes of main group metals, lanthanides, and transition metals, as well as strong bases, and Lewis and Brønsted acids have been developed in these fields.³⁵⁻³⁸ Hydroamination proceeds through addition of N-H bond across C-C multiple bond via either inter- or intramolecularly to product the target amine, the addition of N-H is regioselective, and it follows the Markovnikov or anti-Markovnikov rule.³⁹⁻⁴⁴ The regioselectivity control is vital in hydroamination reactions and anti-Markovnikov hydroamination is a great challenge. The first intermolecular anti-Markovnikov hydroamination was reported by Beller using rhodium/phosphine catalyst systems in 1999,⁴⁵ and since then a number of catalytic systems based on ruthenium, copper, titanium, iridium, platinum, zirconium, gold, palladium and rhodium have been developed for anti-Markovnikov addition.⁴⁶⁻⁵⁴ Among them, ruthenium catalysts have been less studied. In this study, the new ruthenium(II)-complexes were readily synthesized by treating the

$[\text{RuCl}_2(p\text{-cymene})]_2$, benzimidazolium salts and Cs_2CO_3 in toluene. The catalytic activity of ruthenium complexes was evaluated in the hydroamination of styrene in ionic liquid.

RESULTS AND DISCUSSION

Synthesis of ruthenium complexes

The benzimidazolium salts **1** as N-heterocyclic carben precursors were readily synthesized according to the procedure reported in literature in high yields.⁵⁵ Then, the N-heterocyclic carben precursors **1** were reacted with ruthenium complex source $[\text{RuCl}_2(p\text{-cymene})]_2$ in presence of Cs_2CO_3 as base in toluene at 110 °C for 7 h to yield NHC-Ru(II)Cl₂(*p*-cymene) complexes (Scheme 1). From reactions of **1a-c** and $[\text{RuCl}_2(p\text{-cymene})]_2$, the chelating ruthenium complexes $[\text{Ru}(\text{II})\text{Cl}_2(\text{NHC})]$ **2a-c** were obtained in 63-78% yield instead of expected $\text{Ru}(\text{II})\text{Cl}_2(\text{NHC})(p\text{-cymene})$ complexes. Treatment of 1-(3,4,5-trimethoxybenzyl)-3-(naphthalen-1-ylmethyl)benzimidazolium chloride **1d** with $[\text{RuCl}_2(p\text{-cymene})]_2$ in refluxing toluene for 7 h afforded the ruthenate complex **2d** in 80% yield. These complexes were obtained as orange-brown crystalline solids in good yields. They are very stable against air and moisture in the solid-state. The new ruthenium complexes were characterized using ¹H NMR and ¹³C NMR spectroscopy and elemental analysis. All results were consistent with the proposed structures. NMR analyses of the complexes **2a-c** showed that the *p*-cymene ligand had been displaced intramolecularly by the phenyl group, not the naphthyl group attached to the N-heterocyclic carbene ligand to form ruthenium chelate complexes. The formation of ruthenium chelate complexes **2a-c** were confirmed by the disappearance of the resonance signals of benzimidazolium NCHN proton and NCHN carbon in NMR spectra. Also, in NMR spectra of **2a-c**, proton and carbon resonance signals for *p*-cymene ligand were not detected. The ¹³C NMR chemical shifts provide a useful diagnostic tool for this type of metal carbene complexes. The characteristic resonance of the carbene carbon was observed at 201.7, 186.5 and 192.3 ppm respectively for **2a-c**, and these values agree with previously reported $[\text{Ru}(\text{II})\text{Cl}_2(\text{NHC})]$ complexes.²⁶ In ¹H NMR spectrum of **2d**, the resonance of NCHN proton of benzimidazolium cation was observed as a singlet at 10.82 ppm. The methyl signals of *p*-cymene ligands appears as a singlet at 2.31 ppm. The methyl signals of isopropyl group were observed as a doublet at 1.37 ppm. The aromatic protons of *p*-cymene ligands were observed as doublet at 5.31 and 5.52 ppm. In ¹³C NMR spectrum of **2d**, the resonance of NCHN carbon of benzimidazolium cation was observed at 153.3 ppm. The aromatic carbons of *p*-cymene ligands were appears at 79.8, 81.7, 96.4 and 101.0 ppm, and these values agree with previously reported ruthenate(II) complexes.⁵⁶ The results obtained from the elemental analysis of the complexes **2a-d** are in agreement with the theoretical requirements of their structures.



Scheme 1. The synthesis of ruthenium(II) complexes

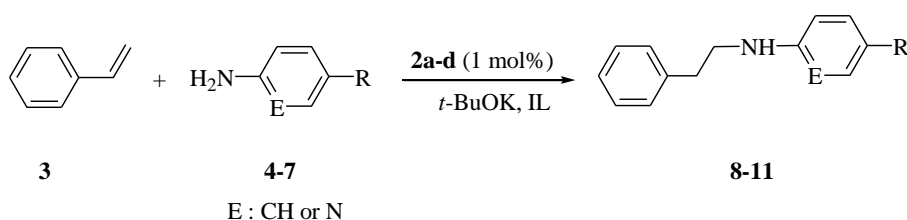
Catalytic studies

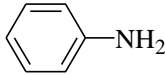
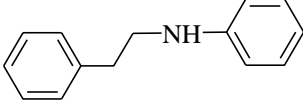
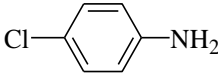
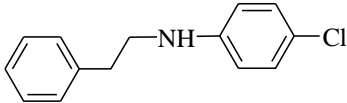
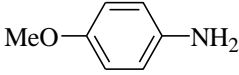
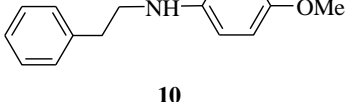
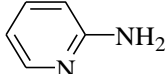
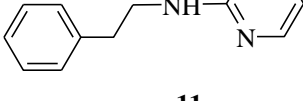
N-Alkylamines can be synthesised by many different methods. The traditional methods for the synthesis of N-alkylamines involve the alkylation of amines with alkylating agents, or the direct reductive amination of aldehydes and ketones using stoichiometric reducing agents.^{57,58} These methods have significant drawbacks, such as toxicity of alkylating and reducing agents, the formation of large amounts of waste, acidic reaction conditions and undesired side products. The hydroamination of alkenes is a convenient method for the synthesis of N-alkylamines, which have versatile applications in polymer materials, pharmaceutical and synthetic industries.⁵⁹⁻⁶¹ In this study, we used the optimized conditions in our previously reported works for the catalytic reactions.⁵³ Potassium *tert*-butoxide (*t*-BuOK) and *N*-butylpyridinium hexafluorophosphate were selected as the base and ionic liquid. The catalytic reactions

were carried out using 1 mol% of ruthenium complexes **2a-d**, 1.10 mmol *t*-BuOK, 1.10 mmol styrene and 1.00 mmol aniline in 1 mL *N*-butylpyridinium hexafluorophosphate at 160 or 185 °C for 1 or 2 h. The hydroamination of styrene with aromatic amines (aniline, 4-chloroaniline, 4-methoxyaniline and 2-aminopyridine) were investigated using precatalysts **2a-d** to obtain the phenethylamines under these reaction conditions. All substrates gave complete anti-Markovnikov regioselectivity, and in all cases, only the anti-Markovnikov products were formed. The characterizations of the products were made by NMR. The yields were based on the corresponding aromatic amine. The conversions were screened by GC analysis and results were presented in Table 1.

Initially, the reaction of styrene (**3**) with aniline (**4**) was tested under the optimized conditions in the presence of complexes **2a-d** as catalysts. As shown in Table 1, all of these reactions gave only the anti-Markovnikov hydroamination product, *N*-(2-phenylethyl)aniline (**8**) in high yields for all four catalysts (Table 1, entries 1-4). No formation of the Markovnikov product was detected in these reactions. Then, the reactions of styrene (**3**) with *p*-chloroaniline (**5**), *p*-methoxyaniline (**6**) and 2-aminopyridine (**7**) were tested under the same reaction conditions in the presence of complexes **2a-d** (Table 1, entries 5-16). The treatment of styrene with *p*-chloroaniline (**5**) (Table 1, entries 5-8) gave *N*-(2-phenylethyl)-4-chloroaniline (**9**) 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 1, entries 9-16). These results clearly show that the electron-donating substituent (*p*-methoxy) on aniline gave slightly lower yield when compared aniline itself. When compared catalytic activities of the complexes **2a-d**, there is no significant difference between ruthenium chelate complexes **2a-c**, and ruthenate complex **2d** in the intermolecular hydroamination of styrene. Also, we observed that the Ru-NHC complexes had more activity than Pd- and Rh-NHC complexes for the intermolecular hydroamination of styrene.^{55,62,63}

Table 1. Hydroamination of styrene using aromatic amines by **2a-d**^{a-c}



Entry	Ar-NH ₂	Catalyst	Product	Yield (%)
1		2a		95
2		2b		94
3		2c		91
4	4	2d		8
5		2a		94
6		2b		97
7		2c		98
8	5	2d		9
9		2a		79
10		2b		85
11		2c		87
12	6	2d		10
13		2a		82 ^d
14		2b		92 ^d
15		2c		93 ^d
16	7	2d		11

^aReaction conditions: **2a-d** (0.01 mmol), styrene (1.10 mmol), aromatic amine (1.00 mmol), *t*-BuOK (1.10 mmol), *N*-butylpyridinium hexafluorophosphate (1 mL). ^bYields were determined GC, dodecane was used as internal standard, products were characterized by NMR. ^c160 °C, 1 h. ^d185 °C, 2 h.

CONCLUSION

From reactions of benzimidazolium salts (**1a-d**) and [RuCl₂(*p*-cymene)]₂, three ruthenium chelate complexes (**2a-c**) and one ruthenate complex (**2d**) were prepared. Upon reaction with [RuCl₂(*p*-cymene)]₂, the benzimidazol-2-ylidene ligands bearing benzylic group with methyl substituents displace the *p*-cymene ligand to give ruthenium chelate complexes, but the benzimidazol-2-ylidene ligand bearing benzylic group with methoxy substituents give the ruthenate complex. These complexes were characterized by elemental analysis and spectroscopic methods. The catalytic activity of the ruthenium(II) complexes was evaluated in the intermolecular hydroamination reaction of styrene with aromatic amines in ionic liquid. The hydroamination reactions proceeded in good to excellent yield with regioselectivity and in all cases, only the anti-Markovnikov addition products were obtained. The formation of the Markovnikov or hydroarylation products were not observed in these reactions.

EXPERIMENTAL

All preparative reactions for the ruthenium complexes (**2a-d**) 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, Et₂O (Na/K alloy), CH₂Cl₂ (P₄O₁₀), 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.⁵⁵ All ¹H and ¹³C NMR spectra were recorded in CDCl₃ using a Bruker AC300P FT spectrometer operating at 300.13 (¹H) or 75.47 MHz (¹³C). 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 μ m 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 halide (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. Et₂O (10 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with Et₂O and dried under vacuum. The crude product was recrystallized from EtOH/ Et₂O.

Synthesis of ruthenium(II)-NHC complexes, **2**

A suspension of benzimidazolium salt (1.10 mmol), Cs₂CO₃ (1.20 mmol) and [RuCl₂(*p*-cymene)]₂ (0.5 mmol) in toluene (20 mL) was stirred at reflux for 7 h. Then, reaction mixture was filtered while hot, and the volume was reduced to about 10 mL before addition of hexane (15 mL). The precipitate formed was crystallized from CH₂Cl₂/ Et₂O to give of orange-brown crystals.

Dichloro-[1-(η^6 -4-methylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]ruthenium(II) (**2a**)

Yield: 63%, mp 277-278 °C. ¹H NMR (CDCl₃) δ : 2.12 (s, 3H, CH₂C₆H₄CH₃-4), 4.00 and 4.04 (d, 2H, J = 12 Hz, CH₂C₆H₄CH₃-4), 4.61 and 5.78 (d, 2H, J = 5.7 Hz, CH₂C₁₀H₇), 6.51-8.29 (m, 11H, NC₆H₄N and CH₂C₁₀H₇). ¹³C NMR (CDCl₃) δ : 20.9 (CH₂C₆H₄CH₃-4), 47.3 (CH₂C₆H₄CH₃-4), 50.5 (CH₂C₁₀H₇), 75.7, 85.3, 107.4 and 109.7 (CH₂C₆H₄CH₃-4), 120.7, 121.0, 122.4, 123.5, 124.7, 124.8, 126.2, 127.6, 128.3, 133.4, 134.0, 134.5, 135.2, 135.8, 136.4 and 139.1 (NC₆H₄N and CH₂C₁₀H₇), 201.7 (Ru-C_{carbene}). Anal.

Calcd for C₂₆H₂₂N₂Cl₂Ru: C, 58.43; H, 4.15; N, 5.24. Found: C, 58.51; H, 4.10; N, 5.18.

Dichloro-[1-(η^6 -2,4,6-trimethylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]-ruthenium(II) (2b)

Yield: 74%, mp 316-317 °C. ¹H NMR (CDCl₃) δ : 2.23 and 2.36 (s, 9H, CH₂C₆H₂(CH₃)_{3-2,4,6}), 5.09 (s, 2H, CH₂C₆H₂(CH₃)_{3-2,4,6}), 5.64 (s, 2H, CH₂C₁₀H₇), 6.40 (s, 2H, CH₂C₆H₂(CH₃)_{3-2,4,6}), 6.81-8.46 (m, 11H, NC₆H₄N and CH₂C₁₀H₇). ¹³C NMR (CDCl₃) δ : 16.9 and 20.9 (CH₂C₆H₂(CH₃)_{3-2,4,6}), 49.1 (CH₂C₆H₂(CH₃)_{3-2,4,6}), 55.4 (CH₂C₁₀H₇), 91.1, 93.3, 97.5 and 101.9 (CH₂C₆H₂(CH₃)_{3-2,4,6}), 111.8, 112.1, 122.2, 123.5, 123.9, 124.1, 124.9, 125.6, 125.7, 126.2, 126.6, 128.0, 128.9, 129.7, 130.9, 133.1, 133.6, 134.5, 135.8 and 136.0 (NC₆H₄N and CH₂C₁₀H₇), 186.5 (Ru-C_{carbene}). Anal. Calcd for C₂₈H₂₆N₂Cl₂Ru: C, 59.79; H, 4.66; N, 4.98. Found: C, 59.86; H, 4.61; N, 4.93.

Dichloro-[1-(η^6 -2,3,4,5,6-pentamethylbenzyl)-3-(naphthalen-1-ylmethyl)benzimidazol-2-ylidene]-ruthenium(II) (2c)

Yield: 78%, mp 259-260 °C. ¹H NMR (DMSO-*d*₆) δ : 2.12, 2.17 and 2.51 (s, 15H, CH₂C₆(CH₃)_{5-2,3,4,5,6}), 5.28 and 5.72 (s, 2H, CH₂C₆(CH₃)_{5-2,3,4,5,6}), 5.75 and 6.13 (s, 2H, CH₂C₁₀H₇), 6.84-8.14 (m, 11H, NC₆H₄N and CH₂C₁₀H₇). ¹³C NMR (DMSO-*d*₆) δ : 16.9, 17.5 and 20.9 (CH₂C₆(CH₃)_{5-2,3,4,5,6}), 55.4 (CH₂C₆(CH₃)_{5-2,3,4,5,6}), 65.3 (CH₂C₁₀H₇), 91.1, 93.2, 97.6 and 102.2 (CH₂C₆(CH₃)_{5-2,3,4,5,6}), 108.7, 112.4, 112.8, 116.1, 116.3, 121.2, 124.2, 124.7, 126.3, 128.7, 130.1, 131.4, 133.1 and 138.3 (NC₆H₄N and CH₂C₁₀H₇), 192.3 (Ru-C_{carbene}). Anal. Calcd for C₃₀H₃₀N₂Cl₂Ru: C, 61.01; H, 5.12; N, 4.74. Found: C, 61.08; H, 5.17; N, 4.81.

1-(3,4,5-Trimethoxybenzyl)-3-(naphthalen-1-ylmethyl)benzimidazolium trichlorido(*p*-cymene)ruthenate(II) (2d)

Yield: 80%, mp 238-239 °C. ¹H NMR (CDCl₃) δ : 1.37 (d, *J* = 6.9 Hz, 6H, H₃CC₆H₄CH(CH₃)₂), 2.31 (s, 3H, H₃CC₆H₄CH(CH₃)₂), 3.18 (h, *J* = 6.9 Hz, 1H, H₃CC₆H₄CH(CH₃)₂), 3.79 and 3.82 (s, 9H, CH₂C₆H₂(OCH₃)_{3-3,4,5}), 5.31 and 5.52 (d, *J* = 6.9 Hz, 4H, H₃CC₆H₄CH(CH₃)₂), 6.51 (s, 2H, CH₂C₆H₂(OCH₃)_{3-3,4,5}), 5.92 (s, 2H, CH₂C₁₀H₇); 6.75 (s, 2H, CH₂C₆H₂(OCH₃)_{3-3,4,5}), 7.21-8.32 (m, 11H, NC₆H₄N and CH₂C₁₀H₇), 10.82 (s, 1H, NCHN). ¹³C NMR (CDCl₃) δ : 18.8, 22.3 and 30.2 (H₃CC₆H₄CH(CH₃)₂), 79.8, 81.7, 96.4 and 101.0 (H₃CC₆H₄CH(CH₃)₂), 56.6 and 60.8 (CH₂C₆H₂(OCH₃)_{3-3,4,5}), 50.4 (CH₂C₁₀H₇), 52.0 (CH₂C₆H₂(OCH₃)_{3-3,4,5}), 113.5, 114.0, 123.4, 125.1, 126.2, 126.3, 127.0, 127.4, 128.9, 129.1, 129.3, 129.6, 130.9, 131.4, 131.7, 133.8 and 138.1 (Ar-C), 153.3

(NCHN). Anal. Calcd for C₃₈H₄₁N₂Cl₃O₃Ru: C: 58.43, H: 5.29, N: 3.59. Found: C: 58.52, H: 5.33, N: 3.51.

General procedure for the hydroamination of styrene

The Ru-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 or 185 °C 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 Na₂SO₄ 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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