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Ruthenium(II)-(*p*-cymene)-*N*-Heterocyclic Carbene Complexes for the *N*-Alkylation of Amine Using the Green Hydrogen Borrowing Methodology

Murat Kaloğlu,[a,b] Nevin Gürbüz,[a,b] David Sémeril[c] and İsmail Özdemir*[a,b]

Dedication ((optional))

Abstract: Six ruthenium(II) complexes with the general molecular formula [$RuCl_2$(NHC)(η^6-*p*-cymene)] (NHC = *N*-heterocyclic carbene) were synthesized by the transmetalation method from [$RuCl_2$(η^6-*p*-cymene)]$_2$ and silver(I)-NHC complexes. All complexes were fully characterized by analytical and spectral methods (FT-IR, elemental analysis and ^{1}H and ^{13}C NMR). The solid-state structure of one of the ruthenium complexes {dichloro-[1-(2-(2-ethoxyphenoxy)ethyl)-3-(3,5-dimethylbenzyl)benzimidazol-2-ylidene](*p*-cymene) ruthenium(II)} has been established by single-crystal X-ray diffraction study, which revealed that the ruthenium atom adopt a classical piano-stool coordination geometry. Under the optimised conditions, these ruthenium complexes were found to be efficient catalysts for *N*-alkylation of aniline with arylmethyl alcohols using the hydrogen borrowing strategy, which is a cost-effective and environmentally attractive reaction for the preparation of *N*-alkylated amines.

Introduction

Alkyl amines are widely used in both the bulk and fine chemical industries as biologically active compounds, agrochemicals, functionalized materials and dyes [1]. Due to the importance of these products, alkylation of primary amines to secondary or tertiary amines is one of the most fundamental and important reactions in organic chemistry [2]. Alkylated amines are traditionally synthesized by using alkylating agents, such as alkyl halides in the presence of stoichiometric amounts of inorganic bases. However, these procedures are often associated with environmental problems, such as the toxic nature of alkylating agents. In addition, these reactions generate equimolar amounts of wasteful salts as by-products (Figure 1a) [3]. Thus, valuable methods have been developed for the catalytically synthesis of secondary or tertiary amines, including Buchwald-Hartwig [4], Ullmann [5], hydroamination [6] and hydroaminovinylation [7]. In this context, the creation of C-N bonds from primary or secondary amines and alcohols as alkylating agent using the "*hydrogen borrowing*" or "*hydrogen auto-transfer*" methodology has more recently attracted attention (Figure 1b) [8]. In this one-pot reaction, the alcohol is dehydrogenated *in situ* to give the corresponding aldehyde or ketone by the catalyst, which "*borrows*" hydrogen from the substrate. Subsequent condensation with the amine and final rehydrogenation leads to alkylated amine. This transformation is highly atom economical and environmentally friendly, since water was produced as the only by-product.

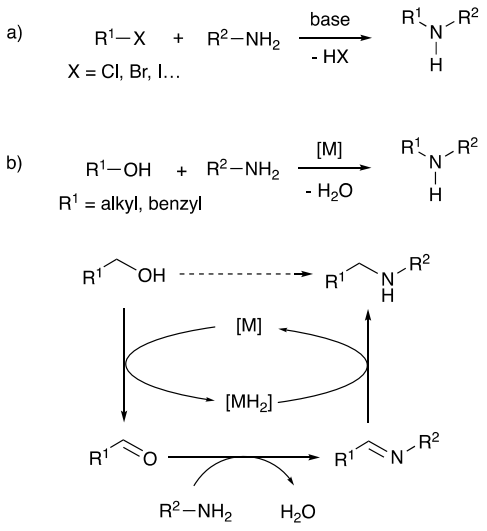

Figure 1. (a) Traditional approach using alkyl halides and (b) hydrogen borrowing strategy for C-N bond formation.

At the beginning of the 1980s, pioneering reports dealing with the rhodium and ruthenium catalysed *N*-alkylation of amines by alcohols were described independently by the groups of Grigg ([$RhH(PPh_3)_4$]) [9], Watanabe ([$RuCl_2(PPh_3)_3$]) [10] and Murahashi ([$RuH_2(PPh_3)_4$]) [11]. These first reports demonstrated that noble metals such as rhodium, ruthenium could catalyse the hydrogen borrowing reaction, but with a lack

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of selectivity, formation of both secondary and tertiary amines, due to the harsh catalytic conditions. Then new catalysts were developed to carry out this reaction under milder conditions, especially lower temperature [12]. Recent of applications catalysed by mainly ruthenium- or iridium-based complexes have been described by the groups of Williams [13], Fujita [14], Crabtree [15], Peris [16], Beller [17], Zhao [18], Wang [19],and from other groups [20].

Over the last 20 years, *N*-heterocyclic carbenes (NHCs) have become an ubiquitous alternative to phosphine ligands in homogeneous catalysis [21] in particularly in association with ruthenium salts [22], which have been reported to be active catalysts for the *N*-alkylation of amines with alcohols by hydrogen borrowing strategy [23].

In a recent study we have reported the synthesis of benzimidazolium salts and their silver(I) complexes, which were tested as potential antimicrobial agents [24]. In the present article, we now described the synthesis and characterization of two benzimidazolium salts and six novel ruthenium(II) complexes of the general formula $[RuCl_2(NHC)(\eta^6\text{-}p\text{-cymene})]$ **1a-f** (Figure 2). These complexes were tested in *N*-alkylation of aniline with arylmethyl alcohols using the hydrogen borrowing strategy.

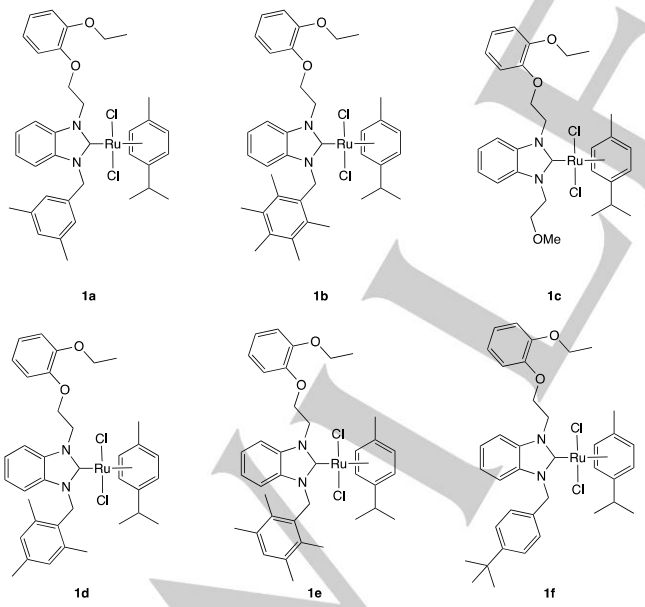


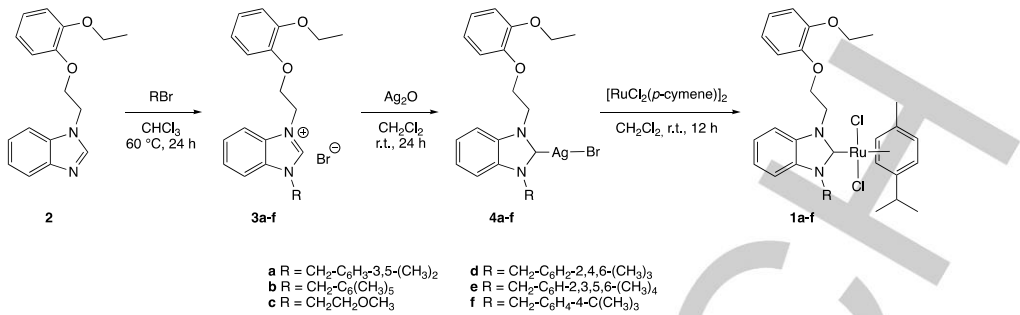
Figure 2. Ruthenium complexes **1a-f** synthesised and assessed in the present study.

Results and Discussion

Preparation of Ruthenium(II) Complexes

The synthesis of ruthenium complexes **1a-f** required that of the benzimidazolium salts **3a-f**, respectively (Scheme 1). The two new benzimidazolium salts **3a** and **3b** were obtained by alkylation (RBr; R = CH_2-C_6H_3-3,5-$(CH_3)_2$ and CH_2-C_6-$(CH_3)_5$) of benzimidazole **2** in 87 and 83 % isolated yield, respectively. The salts **3a** and **3b** were fully characterised by elemental analysis, ^{1}H and ^{13}C NMR and infrared spectroscopies (Table 1). The FT-IR spectra of the free ligands showed a broad band at 1572 and 1556 cm^{-1}, which corresponds to the -C=N- bond vibration of **3a** and **3b**, respectively. The signal of the NC*H*N proton appears in the expected range, at δ = 11.42 and 10.33 ppm for **3a** and **3b**, respectively. Their ^{13}C NMR spectra display the characteristic singlet at 143.1 and 142.1 ppm for the NCHN carbon for **3a** and **3b**, respectively [24, 25]. The silver complexes **4a** and **4b** were synthesized according to the general method described by Wang and Lin [26] by reacting the corresponding benzimidazolium salts with Ag_2O in dichloromethane under dark condition at room temperature for 24 h. The spectroscopic data are similar to those found for other silver(I)-NHC complexes [24, 27]. The two silver(I) complexes exhibit a characteristic $\nu_{(NCN)}$ band at 1442 and 1451 cm^{-1} for **4a** and **4b**, respectively. In their ^{1}H NMR spectra, the NC*H*N protons were disappeared upon complexation with silver. As previously mentioned by several authors [28], the Ag-C atom was not observed by ^{13}C NMR spectroscopy in complexes **4a** and **4b**. Note that, benzimidazolium salts **3c-f** and their corresponding silver complexes **4c-f** were conveniently prepared according to a method reported earlier [24].

The ruthenium(II) arene complexes **1a-f** were obtained in 57-70 % yields by transmetalation of the corresponding silver adducts **4a-f** and $[RuCl_2(p\text{-cymene})]_2$ (Scheme 1). The air- and moisture-stable ruthenium complexes are brown in colour and soluble in common chlorinated organic solvents. They are found to be diamagnetic and they were fully characterised by elemental analysis, ^{1}H and ^{13}C NMR and infrared spectroscopies (Table 1). Their FT-IR data each show a band at 1450-1454 cm^{-1} ($\nu_{(NCN)}$) and their ^{13}C NMR spectra each display a singlet in the range 189.9-191.5 ppm (N*C*N), two evidences of the formation of a Ru-carbene bond [29].



Scheme 1. Synthesis of ruthenium complexes **1a-f**.

Table 1. Physical and spectroscopic properties of new compounds.

Compound	Formula	Isolated yield (%)	M.p. (°C)	*ν*(CN) (cm^{-1})	H(2) ^{1}H NMR (ppm)	C(2) ^{13}C NMR (ppm)
3a	$C_{26}H_{29}BrN_2O_2$	87	178-179	1572	11.42	143.1
3b	$C_{29}H_{35}BrN_2O_2$	83	169-170	1556	10.33	142.1
4a	$C_{26}H_{28}AgBrN_2O_2$	81	206-207	1442	-	not observed[a]
4b	$C_{29}H_{34}AgBrN_2O_2$	74	151-152	1451	-	not observed[a]
1a	$C_{36}H_{42}RuCl_2N_2O_2$	65	187-188	1452	-	191.2
1b	$C_{39}H_{48}RuCl_2N_2O_2$	57	165-166	1450	-	189.9
1c	$C_{30}H_{38}RuCl_2N_2O_3$	62	136-137	1452	-	190.6
1d	$C_{37}H_{44}RuCl_2N_2O_2$	70	191-192	1450	-	190.2
1e	$C_{38}H_{46}RuCl_2N_2O_2$	63	157-158	1454	-	189.9
1f	$C_{38}H_{46}RuCl_2N_2O_2$	68	159-160	1452	-	191.5

[a] As previously reported by several groups [26], for compounds **4a** and **4b**, the characteristic C-Ag picks were not observed.

Structural Characterization of Complex 1a

The solid-state structure of the mononuclear ruthenium complex **1a** was established by a single-crystal X-ray diffraction study (Figure 3 and Table 2). The complex crystallised with one molecule of chloroform. The half-sandwich arene ruthenium(II) complex adopts a classical piano-stool geometry with a typical Ru-$C_{carbene}$ bond length (2.060(4) Å) [29].

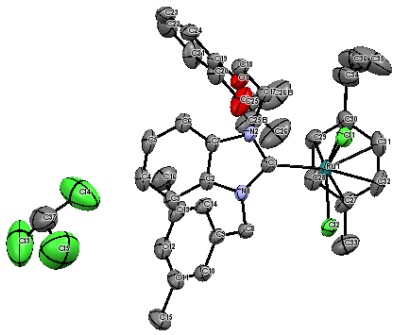


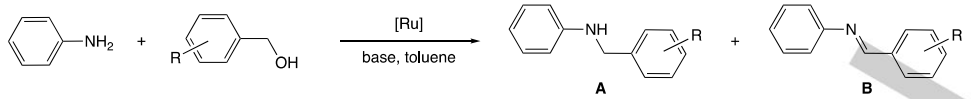
Figure 3. ORTEP drawing illustrating the solid state structure of complex **1a**•$CHCl_3$ (displacement ellipsoids are drawn at the 50 % probability level).

Table 2. Selected bond lengths [Å] and angles [°] in complex **1a**•$CHCl_3$.

	Lengths [Å]		Angles [°]
C(1)-Ru(1)	2.060(4)	N(1)-C(1)-Ru(1)	126.6(3)
Cl(1)-Ru(1)	2.420(1)	N(2)-C(1)-Ru(1)	128.2(3)
Cl(2)-Ru(1)	2.429(1)	Cl(1)-Ru(1)-Cl(2)	84.15(4)
C(1)-N(1)	1.365(6)	N(1)-C(1)-N(2)	105.1(3)
C(1)-N(2)	1.365(4)	C(1)-N(1)-C(8)	127.1(3)
C(8)-N(1)	1.459(5)	C(1)-N(2)-C(17)	126.5(3)
C(17)-N(2)	1.464(6)	C(1)-Ru(1)-C(l1)	89.4(1)
		C(1)-Ru(1)-C(l2)	87.5(1)

N-Alkylation of Aniline with Arylmethyl Alcohols

The ruthenium complexes **1a-f** were evaluated as catalysts for *N*-alkylation of aniline with arylmethyl alcohols. The corresponding tests were performed in the presence of a base in toluene at 120 °C for 24 hour. In the present catalytic conditions, two products may be formed, namely, a *N*-(arylmethyl)aniline (**A**) or a *N*-phenyl-arylmethylanimine (**B**) (Scheme 2).



Scheme 2. *N*-alkylation of aniline with arylmethyl alcohol.

To determine the optimal catalytic conditions, ruthenium complex **1c** (5 mol %) was used in the alkylation of aniline with benzyl alcohol at 120 °C in toluene. Each experiment was stopped after 24 h. As a control experiment, no products were formed without the addition of ruthenium complex (Table 3, entry 1). In the first series of reactions, we determined the optimal base by employing either ^{t}BuOK, Cs_2CO_3 or KOH. As can be inferred from the results (Table 3, entries 2-4), the most efficient base was ^{t}BuOK, which led to a full conversion with an **A**/**B** ratio of 85/15. Reducing the catalyst loading to 1 mol % decreased the conversion and the selectivity toward the formation of compound **A** (Table 3, entries 4 and 5). A good compromise is the use of 2.5 mol % of **1c**, which led to a full conversion after 24 h with an **A**/**B** ratio of 80/20 (Table 3, entry 6). Operating at lower temperature or for a shorter time reduced both the conversion and the chemoselectivity (Table 3, entries 7 and 8). Note that, under our catalytic conditions, only mono-alkylated compounds were formed, no bis-alkylated derivatives were observed.

Table 3. *N*-alkylation of aniline with benzyl alcohol – a search for optimal catalytic conditions.[a]

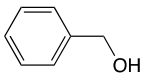
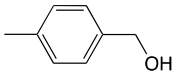
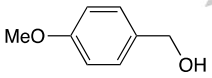
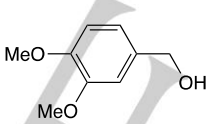
Entry	**1c** [mol %]	Base	Time [h]	Temp. [°C]	Yield [%]	Selectivity [%]	
						A	**B**
1	No	^{t}BuOK	24	120	0	-	-
2	5	Cs_2CO_3	24	120	32	89	11
3	5	KOH	24	120	71	72	28
4	5	^{t}BuOK	24	120	100	85	15
5	1	^{t}BuOK	24	120	70	70	30
6	2.5	^{t}BuOK	24	120	100	80	20
7	2.5	^{t}BuOK	16	120	80	69	31
8	2.5	^{t}BuOK	24	90	74	73	27

[a] Reagents and conditions: **1c**, benzyl alcohol (1.0 mmol), aniline (1.1 mmol), base (2.5 mmol), toluene (3 mL). The conversions and the selectivities were determined by GC and GC-MS analysis with the calibrations based on dodecane.

Under the determined optimal conditions, ^{t}BuOK as base in toluene at 120 °C for 24 h, the ruthenium complexes **1a-f** (2.5 mol %) were further examined in the *N*-alkylation of aniline with four arylmethyl alcohols, namely, benzyl alcohol, *p*-tolylmethanol, (4-methoxyphenyl)methanol and (3,4-dimethoxyphenyl)methanol (Table 4). In all tests, conversions in arylmethyl alcohol higher than 78 % were measured. Due to the similar nature of the NHC moieties, small differences in reactivities were observed. Nevertheless, by comparison with common NHCs such as 1,3-bis(2,4,6-trimethylphenyl)imidazolylidene [22f], the presence of benzimidazolylidene contributes to promote the formation of amines **A** rather than imines **B**.

The two more efficient ruthenium precatalysts were complexes **1c** and **1d**. With the latter complexes, full conversions were reached for benzyl alcohol (**1c**), *p*-tolylmethanol (**1d**) and (4-methoxyphenyl)methanol (**1d**) (Table 4, entries 3, 10 and 16). A conversion of 95 % for the more sterically hindered (3,4-dimethoxyphenyl)methanol was observed when ruthenium complex **1e** was employed (Table 4, entry 23). In all catalysis, high chemoselectivities toward the formation of amines **A** were obtained. In fact, **A**/**B** ratios of 95/5 were measured for alkylation with benzyl alcohol and *p*-tolylmethanol when complexes **1a** and **1f** were used, respectively (Table 4, entries 1 and 12). For the two alcohols bearing methoxy substituents, (4-methoxyphenyl)methanol (**A**/**B** = 97/3) and (3,4-dimethoxyphenyl)methanol (**A**/**B** = 94/6), the highest selectivity for the formation of amine products was obtained with complex **1e** (Table 4, entries 17 and 23).

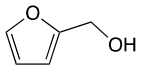
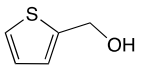
Table 4. Ruthenium-catalysed *N*-alkylation of aniline with arylmethyl alcohols.[a]

Entry	[Ru] complex	Arylmethyl alcohol	Yield [%]	Selectivity [%]	
				A	**B**
1	**1a**		91	95	5
2	**1b**		86	76	24
3	**1c**		100	80	20
4	**1d**		91	93	7
5	**1e**		96	89	11
6	**1f**		80	80	20
7	**1a**		88	72	28
8	**1b**		94	80	20
9	**1c**		87	83	17
10	**1d**		100	92	8
11	**1e**		92	83	17
12	**1f**		100	95	5
13	**1a**		90	92	8
14	**1b**		78	78	22
15	**1c**		86	76	24
16	**1d**		100	87	13
17	**1e**		93	97	3
18	**1f**		98	93	7
19	**1a**		89	83	17
20	**1b**		87	77	23
21	**1c**		92	83	17
22	**1d**		89	88	12
23	**1e**		95	94	6
24	**1f**		91	90	10

[a] Reagents and conditions: [Ru] (0.025 mmol, 2.5 mol %), arylmethyl alcohol (1.0 mmol), aniline (1.1 mmol), ^{t}BuOK (2.5 mmol), toluene (3 mL), 120 ^{o}C, 24 h. The conversions and the selectivities were determined by GC and GC-MS analysis with the calibrations based on dodecane.

Ruthenium complexes **1a-f** were further assessed in the *N*-alkylation of aniline with furfuryl alcohol or 2-thiophene methanol (Table 5). Both alcohols were efficiently converted in 24 h when the reactions were performed in the presence of complexes **1c** (99 % for furfuryl alcohol and 97 % for 2-thiophene methanol; Table 5, entries 3 and 9). With the latter precatalyst, the proportions of amines products **A** formed were 91 % with furfuryl alcohol and 98 % with 2-thiophene methanol. Repeating the run with furfuryl alcohol and complex **1f** increase the chimioselectivity toward the formation of **A** to 93 % (Table 5, entry 6).

Table 5. Ruthenium-catalysed *N*-alkylation of aniline with heteroaromatic alcohols.[a]

Entry	[Ru] complex	Heteroaromatic alcohols	Yield [%]	Selectivity [%]	
				A	B
1	1a		100	88	12
2	1b		88	84	16
3	1c		99	91	9
4	1d		95	91	9
5	1e		95	80	20
6	1f		91	93	7
7	1a		92	78	22
8	1b		89	87	13
9	1c		97	98	2
10	1d		90	83	17
11	1e		91	95	5
12	1f		87	78	22

[a] Reagents and conditions: [Ru] (0.025 mmol, 2.5 mol %), heteroaromatic alcohol (1.0 mmol), aniline (1.1 mmol), ^{t}BuOK (2.5 mmol), toluene (3 mL), 120 ^{o}C, 24 h. The conversions and the selectivities were determined by GC and GC-MS analysis with the calibrations based on dodecane.

Conclusions

In this study, we prepared six new ruthenium complexes in which a nitrogen atom of the *N*-heterocyclic carbene ligand is substituted either with an ether or an arylmethyl chain. These complexes were all found to be suitable for *N*-alkylation of aniline with a range of alcohols including arylmethyl alcohols and heteroaromatic alcohols. Future work will aim at exploiting the stabilisation of active species with such ligands in catalytic applications.

Experimental Section

General Methods: All reactions performed to prepare the benzimidazolium salts and their metal complexes were carried out under argon in flame-dried glassware using standard Schlenk techniques. Chemicals and solvents were purchased from Sigma-Aldrich and Merck. Dichloromethane, dimethylformamide, toluene and diethyl ether were of anhydrous quality and were used as received. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon. All reagents were purchased from commercial sources and used without further purification. Microanalyses were performed by İnönü University Scientific and Technological Research Center (Malatya, Turkey). IR spectra were recorded on ATR unit in the range of 400-4000 cm^{-1} with Perkin Elmer Spectrum 100 Spectrofotometer. Melting points were measures in open capillary tubes with an Electrothermal-9200 melting points apparatus. Routine ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance AMX spectrometer operating at 300, 400 and 500 MHz for ^{1}H NMR, and at 75, 100 and 125 MHz for ^{13}C NMR in $CDCl_3$ with tetramethylsilane as an internal reference. The NMR studies were carried out in high-quality 5 mm NMR tubes. Chemical shifts (δ) and coupling constants (J) are reported in ppm and in Hz, respectively. ^{1}H NMR spectra are referenced to residual protiated solvents (δ = 7.26 ppm for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuteriated solvents (δ = 77.16 ppm for $CDCl_3$). The catalytic solutions were analysed with an Agilent 6890N GC and Schimadzu 2010 Plus GC-MS system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter, and 0.25 μm film thickness. The benzimidazolium bromides **3c-f** and the silver(I) complexes **4c-f** were prepared according to literature procedures [24].

General Procedure for the Preparation of Benzimidazolium Bromides 3a and 3b: A chloroform (10 mL) solution of *1*-(2-(2-ethoxyphenoxy)ethyl)benzimidazole (0.282 g, 1.0 mmol) and alkyl bromide (1.0 mmol) was stirred at 60 °C for 24 h. After completion of the reaction, the solvent was removed by vacuum and diethyl ether (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with Et_2O (3 × 10 mL) and dried under vacuum. The crude product was recrystallized from EtOH/Et_2O mixture (1:2, *v/v*) and dried under vacuum.

1-(2-(2-Ethoxyphenoxy)ethyl)-3-(3,5-dimethylbenzyl)benzimidazolium Bromide 3a: (0.480 g, yield 87 %) ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.33 (t, ^{3}J = 7.0 Hz, 3H, OCH_2CH_3), 2.27 (s, 6H, $C_6H_3(CH_3)_2$), 3.95 (q, ^{3}J = 6.9 Hz, 2H, OCH_2CH_3), 4.56 (t, ^{3}J = 4.5 Hz, 2H, NCH_2CH_2O), 5.25 (t, ^{3}J = 4.4 Hz, 2H, NCH_2CH_2O), 5.69 (s, 2H, $NCH_2C_6H_3(CH_3)_2$), 6.80-6.90 (m, 4H, arom. CH, $C_6H_4OCH_2CH_3$), 6.97 (s, 1H, arom. CH, $C_6H_3(CH_3)_2$), 7.05 (s, 2H, arom. CH, $C_6H_3(CH_3)_2$), 7.54-7.61 (m, 3H, arom. CH, C_6H_4 benzimidazol), 8.22 (d, ^{3}J = 6.0 Hz, 1H, arom. CH, C_6H_4 benzimidazol), 11.42 (s, 1H, NCHN) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 14.9 (s, OCH_2CH_3), 21.2 (s, $C_6H_3(CH_3)_2$), 47.9 (s, OCH_2CH_3), 51.7 (s, NCH_2CH_2O), 63.8 (s, NCH_2CH_2O), 68.2 (s, $NCH_2C_6H_3(CH_3)_2$), 112.7-148.7 (arom. *C*s), 143.1 (s, NCHN) ppm.

Elemental analysis calcd (%) for $C_{26}H_{29}BrN_2O_2$ (Mr = 481.42): C 64.87, H 6.07, N 5.82; found (%): C 64.90, H 6.10, N 5.84.

1-(2-(2-Ethoxyphenoxy)ethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium Bromide 3b: (0.435 g, yield 83 %) ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.34 (t, ^3J = 6.8 Hz, 3H, OCH_2CH_3), 2.26 (s, 6H, $NCH_2C_6(CH_3)_5$), 2.29 (s, 6H, $NCH_2C_6(CH_3)_5$), 2.30 (s, 3H, $NCH_2C_6(CH_3)_5$), 3.95 (q, ^3J = 6.8 Hz, 2H, OCH_2CH_3), 4.51 (t, ^3J = 4.0 Hz, 2H, NCH_2CH_2O), 5.33 (t, ^3J = 4.0 Hz, 2H, NCH_2CH_2O), 5.70 (s, 2H, $NCH_2C_6(CH_3)_5$), 6.81-6.94 (m, 4H, arom. CH, $C_6H_4OCH_2CH_3$), 7.56-7.66 (m, 3H, arom. CH, C_6H_4 benzimidazol), 8.30 (d, ^3J = 9.0 Hz, 1H, arom. CH, C_6H_4 benzimidazol), 10.33 (s, 1H, NCHN) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 14.9 (s, OCH_2CH_3), 17.1 (s, $NCH_2C_6(CH_3)_5$), 17.2 (s, $NCH_2C_6(CH_3)_5$), 17.4 (s, $NCH_2C_6(CH_3)_5$), 47.6 (s, OCH_2CH_3), 48.1 (s, NCH_2CH_2O), 63.8 (s, NCH_2CH_2O), 68.5 (s, $NCH_2C_6(CH_3)_5$), 112.5-148.6 (arom. Cs), 142.1 (NCHN) ppm. Elemental analysis calcd (%) for $C_{29}H_{35}BrN_2O_2$ (Mr = 523.50): C 66.53, H 6.74, N 5.35; found (%): C 66.59, H 6.76, N 5.39.

General Procedure for the Preparation of the Silver(I)-NHC Complexes 4a and 4b: A solution of benzimidazolium bromide (1.0 mmol), Ag_2O (0.5 mmol) and activated 4 Å molecular sieves in anhydrous CH_2Cl_2 (10 mL) was stirred at room temperature for 24 h. The reaction mixture was then filtered through Celite and the solvent was removed under reduced pressure. The resulting solid was washed with Et_2O (3 × 5 mL) and dried under vacuum. The crude product was recrystallized from CH_2Cl_2/ Et_2O (1:2, *v/v*).

Bromo-[1-(2-(2-ethoxyphenoxy)ethyl)-3-(3,5-dimethylbenzyl)benzimidazol-2-ylidene]silver(I) 4a: (0.477 g, yield 81 %) ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.29 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3), 2.18 (s, 6H, $C_6H_3(CH_3)_2$), 3.89 (q, ^3J = 7.0 Hz, 2H, OCH_2CH_3), 4.38 (t, ^3J = 4.9 Hz, 2H, NCH_2CH_2O), 4.80 (t, ^3J = 4.9 Hz, 2H, NCH_2CH_2O), 5.44 (s, 2H, $NCH_2C_6H_3(CH_3)_2$), 6.68-6.83 (m, 4H, arom. CH, $C_6H_4OCH_2CH_3$), 6.82 (s, 2H, arom. CH, $C_6H_3(CH_3)_2$), 6.85 (s, 1H, arom. CH, $C_6H_3(CH_3)_2$), 7.24-7.31 (m, 3H, arom. CH, C_6H_4 benzimidazolylidene), 7.82 (d, ^3J = 8.0 Hz, 1H, arom. CH, C_6H_4 benzimidazolylidene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 15.0 (s, OCH_2CH_3), 21.3 (s, $C_6H_3(CH_3)_2$), 49.6 (s, OCH_2CH_3), 53.5 (s, NCH_2CH_2O), 63.9 (s, NCH_2CH_2O), 69.2 (s, $NCH_2C_6H_3(CH_3)_2$), 111.8-148.8 (arom. Cs and C-Ag) ppm. Elemental analysis calcd (%) for $C_{26}H_{28}AgBrN_2O_2$ (Mr = 588.28): C 53.08, H 4.80, N 4.76; found (%): C 53.10, H 4.82, N 4.79.

Bromo[1-(2-(2-ethoxyphenoxy)ethyl)-3-(2,3,4,5,6-pentamethylbenzyl) benzimidazol-2-ylidene]silver(I) 4b: (0.466 g, yield 74 %) ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.33 (t, ^3J = 6.9 Hz, 3H, OCH_2CH_3), 2.10 (s, 6H, $NCH_2C_6(CH_3)_5$), 2.11 (s, 6H, $NCH_2C_6(CH_3)_5$), 2.14 (s, 3H, $NCH_2C_6(CH_3)_5$), 3.91 (q, ^3J = 6.8 Hz, 2H, OCH_2CH_3), 4.28 (t, ^3J = 4.8 Hz, 2H, NCH_2CH_2O), 4.69 (t, ^3J = 4.8 Hz, 2H, NCH_2CH_2O), 5.38 (s, 2H, $NCH_2C_6(CH_3)_5$), 6.63-6.84 (m, 4H, arom. CH, $C_6H_4OCH_2CH_3$), 7.34-7.43 (m, 3H, arom. CH, C_6H_4 benzimidazolylidene), 7.86 (d, ^3J = 8.0 Hz, 1H, arom. CH, C_6H_4 benzimidazolylidene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 15.0 (s, OCH_2CH_3), 17.1 (s, $NCH_2C_6(CH_3)_5$), 17.2 (s, $NCH_2C_6(CH_3)_5$), 17.2 (s, $NCH_2C_6(CH_3)_5$), 47.5 (s, OCH_2CH_3), 50.3 (s, NCH_2CH_2O), 63.9 (s, NCH_2CH_2O), 69.4 (s, $NCH_2C_6(CH_3)_5$), 110.8-148.7 (arom. Cs and C-Ag) ppm. Elemental analysis calcd (%) for $C_{29}H_{34}AgBrN_2O_2$ (Mr = 630.36): C 55.26, H 5.44, N 4.44; found (%): C 55.27, H 5.46, N 4.45.

General Procedure for the Preparation of the Ruthenium(II)-NHC Complexes 1a-f: To a solution of silver (I) complex (2.0 mmol) in anhydrous CH_2Cl_2 (10 mL) was added $[RuCl_2(p\text{-cymene})]_2$ (1.0 mmol). The reaction mixture was then stirred for 12 h at room temperature, then was filtered through Celite. The filtrate was evaporated under vacuum, the solid residue was washed with Et_2O (3 × 5 mL), dried under vacuum and recrystallized from $CHCl_3$/ Et_2O (1:2, *v/v*).

Dichloro-[1-(2-(2-ethoxyphenoxy)ethyl)-3-(3,5-dimethylbenzyl)benzimidazol-2-ylidene](*p*-cymene) ruthenium(II) 1a: (0.919 g, yield 65 %) ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.24 (d, ^3J = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.46 (t, ^3J = 6.9 Hz, 3H, OCH_2CH_3), 2.04 (s, 3H, CH_3 of *p*-cymene), 2.21 (s, 6H, $C_6H_3(CH_3)_2$), 2.92 (hept, ^3J = 7.0 Hz, 1H, $CH(CH_3)_2$), 4.08 (q, ^3J = 6.9 Hz, 2H, OCH_2CH_3), 4.52-4.56 (m, 2H, NCH_2CH_2O), 4.97-5.04 (m, 1H, NCH_2CH_2O), 5.15 (d, ^3J = 5.6 Hz, 2H, arom. CH of *p*-cymene), 5.30-5.33 (m, 1H, NCH_2CH_2O), 5.40-5.44 (m, 1H, $NCH_2C_6H_3(CH_3)_2$), 5.54-5.59 (m, 2H, arom. CH of *p*-cymene), 6.48-6.52 (m, 1H, $NCH_2C_6H_3(CH_3)_2$), 6.66 (s, 2H, arom. CH, $C_6H_3(CH_3)_2$), 6.80-6.91 (m, 4H, arom. CH, $C_6H_4OCH_2CH_3$), 6.84 (s, 1H, arom. CH, $C_6H_3(CH_3)_2$), 7.03 (d, ^3J = 8.0 Hz, 1H, arom. CH, C_6H_4 benzimidazol), 7.13 (t, ^3J = 8.0 Hz, 1H, arom. CH, C_6H_4 benzimidazol), 7.24 (d, ^3J = 8.0 Hz, 1H, arom. CH, C_6H_4 benzimidazol), 8.08 (d, ^3J = 8.0 Hz, 1H, arom. CH, C_6H_4 benzimidazol) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 15.1 (s, OCH_2CH_3), 18.3 (s, CH_3 of *p*-cymene), 21.3 (s, $CH(CH_3)_2$), 21.4 (s, $CH(CH_3)_2$), 21.6 (s, $C_6H_3(CH_3)_2$), 23.6 (s, $C_6H_3(CH_3)_2$), 30.7 (s, $CH(CH_3)_2$), 50.5 (s, OCH_2CH_3), 52.6 (s, $NCH_2C_6H_3(CH_3)_2$), 63.9 (s, NCH_2CH_2O), 69.6 (s, NCH_2CH_2O), 83.1 (s, arom. CH of *p*-cymene), 85.0 (s, arom. CH of *p*-cymene), 85.1 (s, arom. CH of *p*-cymene), 86.4 (s, arom. CH of *p*-cymene), 98.7-148.8 (arom. Cs), 191.2 (s, C-Ru) ppm. Elemental analysis calcd (%) for $C_{36}H_{42}RuCl_2N_2O_2$ (Mr = 706.70): C 61.18, H 5.99, N 3.96; found (%): C 61.20, H 6.02, N 3.99.

Dichloro-[1-(2-(2-ethoxyphenoxy)ethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazol-2-ylidene](*p*-cymene) ruthenium(II) 1b: (0.854 g, yield 57 %) ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.32 (d, ^3J = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.45 (t, ^3J = 6.8 Hz, 3H, OCH_2CH_3), 2.15 (s, 3H, CH_3 of *p*-cymene), 2.18 (s, 6H, $C_6(CH_3)_5$), 2.20 (s, 6H, $C_6(CH_3)_5$), 2.29 (s, 3H, $C_6(CH_3)_5$), 3.02 (hept, ^3J = 7.0 Hz, 1H, $CH(CH_3)_2$), 4.08 (q, ^3J = 6.8 Hz, 2H, OCH_2CH_3), 4.46-4.56 (m, 2H, NCH_2CH_2O), 5.00-5.08 (m, 1H, NCH_2CH_2O), 5.34-5.75 (m, 6H, NCH_2CH_2O, $NCH_2C_6(CH_3)_5$ and arom. CH of *p*-cymene), 6.13 (d, ^3J = 8.4 Hz, 1H, arom. CH, C_6H_4 benzimidazolylidene), 6.78-6.90 (m, 6H, $NCH_2C_6(CH_3)_5$ and arom. CH of C_6H_4 benzimidazolylidene and $C_6H_4OCH_2CH_3$), 7.08 (t, 1H, ^3J = 8.4 Hz, 1H, arom. CH, C_6H_4 benzimidazolylidene), 7.87 (d, ^3J = 8.4 Hz, 1H, arom. CH, C_6H_4 benzimidazolylidene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 15.1 (s, OCH_2CH_3), 16.9 (s, $NCH_2C_6(CH_3)_5$), 17.2 (s, $NCH_2C_6(CH_3)_5$), 17.4 (s, $NCH_2C_6(CH_3)_5$), 18.6 (s, CH_3 of *p*-cymene), 21.9 (s, $CH(CH_3)_2$), 23.5 (s, $CH(CH_3)_2$), 30.9 (s, $CH(CH_3)_2$), 50.4 (s, OCH_2CH_3), 52.5 (s, $NCH_2C_6(CH_3)_5$), 63.9 (s, NCH_2CH_2O), 69.3 (s, NCH_2CH_2O), 84.9 (s, arom. CH of *p*-cymene), 85.6 (s, arom. CH of *p*-cymene), 86.3 (s, arom.

CH of *p*-cymene), 86.6 (s, arom. CH of *p*-cymene), 98.2-148.8 (arom. *C*s), 189.9 (s, C-Ru) ppm. Elemental analysis calcd (%) for $C_{39}H_{48}RuCl_2N_2O_2$ (Mr = 748.78): C 62.56, H 6.46, N 3.74; found (%): C 62.89, H 6.51, N 3.77.

Dichloro-[1-(2-(2-ethoxyphenoxy)ethyl)-3-(2-methoxyethyl)benzimidazol-2-ylidene](*p*-cymene) ruthenium(II) 1c: (0.802 g, yield 62 %) ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.30 (d, ^3J = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.50 (t, ^3J = 7.0 Hz, 3H, OCH$_2$CH_3), 2.04 (s, 3H, CH_3 of *p*-cymene), 3.04 (hept, ^3J = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 3.34 (s, 3H, OCH_3), 3.88-3.93 (m, 2H, NCH$_2$CH_2OCH$_3$), 4.11 (q, ^3J = 7.0 Hz, 2H, OCH_2CH$_3$), 4.45-4.60 (m, 2H, NCH$_2$CH_2OAr), 4.68-4.77 (m, 1H, NCH_2CH$_2$OCH$_3$), 4.87-5.00 (m, 1H, NCH_2CH$_2$OAr), 5.03-5.13 (m, 1H, NCH_2CH$_2$OAr), 5.27-5.48 (m, 3H, NCH_2CH$_2$OAr and arom. CH of *p*-cymene), 5.56-5.68 (m, 2H, arom. CH of *p*-cymene), 6.84-6.93 (m, 4H, arom. CH, C$_6H_4$OCH$_2$CH$_3$), 7.10-7.14 (m, 2H, arom. CH, C$_6H_4$ benzimidazolylidene), 7.56-7.64 (m, 1H, arom. CH, C$_6H_4$ benzimidazolylidene), 8.02-8.10 (m, 1H, arom. CH, C$_6H_4$ benzimidazolylidene) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 15.0 (s, OCH$_2$CH_3), 18.5 (s, CH_3 of *p*-cymene), 22.3 (s, CH(CH_3)$_2$), 22.7 (s, CH(CH_3)$_2$), 30.7 (s, CH(CH$_3$)$_2$), 50.4 (s, OCH_2CH$_3$), 58.9 (NCH$_2$CH$_2$OCH_3), 64.0 (s, NCH$_2$CH_2OAr), 69.7 (s, NCH$_2$CH$_2$OCH$_3$), 69.7 (s, NCH_2CH$_2$OAr), 72.2 (s, NCH$_2$CH_2OCH$_3$), 83.3 (s, arom. CH of *p*-cymene), 83.7 (s, arom. CH of *p*-cymene), 86.6 (s, arom. CH of *p*-cymene), 86.8 (s, arom. CH of *p*-cymene), 99.5-148.7 (arom. *C*s), 190.6 (s, C-Ru) ppm. Elemental analysis calcd (%) for $C_{30}H_{38}RuCl_2N_2O_3$ (Mr = 646.60): C 55.72, H 5.92, N 4.33; found (%): C 55.78, H 5.95, N 4.35.

Dichloro-[1-(2-(2-ethoxyphenoxy)ethyl)-3-(2,4,6-trimethylbenzyl)-benzimidazol-2-ylidene](*p*-cymene) ruthenium(II) 1d: (1.009 g, yield 70 %) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.31 (d, ^3J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.44 (t, ^3J = 7.0 Hz, 3H, OCH$_2$CH_3), 2.11 (s, 3H, CH_3 of *p*-cymene), 2.12 (s, 6H, C$_6$H$_2$(CH_3)$_3$), 2.27 (s, 3H, C$_6$H$_2$(CH_3)$_3$), 3.01 (hept, ^3J = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 4.07 (q, ^3J = 7.0 Hz, 2H, OCH_2CH$_3$), 4.45-4.52 (m, 2H, NCH$_2$CH_2O), 5.01-5.12 (m, 1H, NCH_2CH$_2$O), 5.29-5.62 (m, 5H, NCH_2CH$_2$O and arom. CH of *p*-cymene), 5.66-5.76 (m, 1H, NCH_2C$_6$H$_2$(CH$_3$)$_3$), 6.36 (d, ^3J = 8.4 Hz, 1H, arom. CH, C$_6H_4$ benzimidazol), 6.62-6.72 (m, 1H, NCH_2C$_6$H$_2$(CH$_3$)$_3$), 6.81 (s, 2H, arom. CH, C$_6H_2$(CH$_3$)$_3$), 6.82-6.91 (m, 5H, arom. CH, C$_6H_4$OCH$_2$CH$_3$ and C$_6H_4$ benzimidazol), 7.14 (t, ^3J = 8.4 Hz, 1H, arom. CH, C$_6H_4$ benzimidazol), 7.88 (d, ^3J = 8.4 Hz, 1H, arom. CH, C$_6H_4$ benzimidazol) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 15.1 (s, OCH$_2$CH_3), 18.5 (s, C$_6$H$_2$(CH_3)$_3$), 20.5 (s, C$_6$H$_2$(CH_3)$_3$), 20.9 (s, CH_3 of *p*-cymene), 22.3 (s, CH(CH_3)$_2$), 22.9 (s, CH(CH_3)$_2$), 30.8 (s, CH(CH$_3$)$_2$), 50.2 (s, OCH_2CH$_3$), 50.8 (s, NCH_2C$_6$H$_2$(CH$_3$)$_3$), 63.9 (s, NCH$_2$CH_2O), 69.3 (s, NCH$_2$CH$_2$O), 83.7 (s, arom. CH of *p*-cymene), 84.6 (s, arom. CH of *p*-cymene), 85.2 (s, arom. CH of *p*-cymene), 86.4 (s, arom. CH of *p*-cymene), 97.8-148.8 (arom. *C*s), 190.2 (s, C-Ru) ppm. Elemental analysis calcd (%) for $C_{37}H_{44}RuCl_2N_2O_2$ (Mr = 720.73): C 61.66, H 6.15, N 3.89; found (%): C 61.69, H 6.20, N 3.92.

Dichloro-[1-(2-(2-ethoxyphenoxy)ethyl)-3-(2,3,5,6-tetramethylbenzyl) benzimidazol-2-ylidene](*p*-cymene) ruthenium(II) 1e: (0.926 g, yield 63 %) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.32 (d, ^3J = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.44 (t, ^3J = 7.0 Hz, 3H, OCH$_2$CH_3), 2.10 (s, 6H, C$_6$H(CH_3)$_4$), 2.16 (s, 3H, CH_3 of *p*-cymene), 2.21 (s, 6H, C$_6$H(CH_3)$_4$), 3.03 (hept, ^3J = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 4.07 (q, ^3J = 7.0 Hz, 2H, OCH_2CH$_3$), 4.45-4.56 (m, 2H, NCH$_2$CH_2O), 5.00-5.07 (m, 1H, NCH_2CH$_2$O), 5.34-5.61 (m, 5H, NCH_2CH$_2$O and arom. CH of *p*-cymene), 5.70-5.79 (m, 1H, NCH_2C$_6$H(CH$_3$)$_4$), 6.62 (d, ^3J = 8.0 Hz, 1H, arom. CH, C$_6H_4$ benzimidazol), 6.79-6.89 (m, 6H, NCH_2C$_6$H(CH$_3$)$_4$ and arom. CH of C$_6H_4$OCH$_2$CH$_3$ and C$_6H_4$ benzimidazol), 7.01 (s, 1H, arom. CH, C$_6H$(CH$_3$)$_4$), 7.10 (t, ^3J = 8.0 Hz, 1H, arom. CH, C$_6H_4$ benzimidazol), 7.89 (d, ^3J = 8.0 Hz, 1H, arom. CH, C$_6H_4$ benzimidazol) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 15.1 (s, OCH$_2$CH_3), 16.2 (s, C$_6$H(CH_3)$_4$), 18.6 (s, CH_3 of *p*-cymene), 20.6 (s, C$_6$H(CH$_3$)$_4$), 21.9 (s, CH(CH_3)$_2$), 22.7 (s, CH(CH_3)$_2$), 30.9 (s, CH(CH$_3$)$_2$), 50.3 (s, OCH$_2$CH$_3$), 51.9 (s, NCH_2C$_6$H(CH$_3$)$_4$), 63.9 (s, NCH$_2$CH$_2$O), 69.4 (s, NCH$_2$CH$_2$O), 83.6 (s, arom. CH of *p*-cymene), 85.0 (s, arom. CH of *p*-cymene), 85.3 (s, arom. CH of *p*-cymene), 86.6 (s, arom. CH of *p*-cymene), 98.2-148.8 (arom. *C*s), 189.9 (s, C-Ru) ppm. Elemental analysis calcd (%) for $C_{38}H_{46}RuCl_2N_2O_2$ (Mr = 734.76): C 62.12, H 6.31, N 3.81; found (%): C 62.15, H 6.29, N 3.78.

Dichloro-[1-(2-(2-ethoxyphenoxy)ethyl)-3-(4-*tert*-butylbenzyl)benzimidazol-2-ylidene](*p*-cymene) ruthenium(II) 1f: (0.998 g, yield 68 %) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.21-1.30 (m, 6H, CH(CH_3)$_2$), 1.28 (s, 9H, C(CH_3)$_3$), 1.45 (t, ^3J = 7.0 Hz, 3H, OCH$_2$CH_3), 2.04 (s, 3H, CH_3 of *p*-cymene), 2.89 (hept, ^3J = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 4.10 (q, ^3J = 7.0 Hz, 2H, OCH_2CH$_3$), 4.54-4.56 (m, 2H, NCH$_2$CH_2O), 5.05-5.09 (m, 1H, NCH_2CH$_2$O), 5.17-5.21 (m, 2H, arom. CH of *p*-cymene), 5.31-5.40 (m, 2H, arom. CH of *p*-cymene), 5.57-5.64 (m, 2H, NCH_2CH$_2$O and NCH_2C$_6$H$_4$C(CH$_3$)$_3$), 6.54-6.62 (m, 1H, NCH_2C$_6$H$_4$C(CH$_3$)$_3$), 6.83-7.38 (m, 11H, arom. CH of NCH$_2$C$_6H_4$C(CH$_3$)$_3$, C$_6H_4$OCH$_2$CH$_3$ and C$_6H_4$ benzimidazol), 8.04 (d, ^3J = 8.4 Hz, 1H, arom. CH, C$_6H_4$ benzimidazol) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 15.1 (s, OCH$_2$CH_3), 18.4 (s, CH_3 of *p*-cymene), 21.7 (s, CH(CH_3)$_2$), 23.4 (s, CH(CH_3)$_2$), 30.6 (s, CH(CH$_3$)$_2$), 31.3 (s, C(CH_3)$_3$), 34.5 (s, C(CH$_3$)$_3$), 50.4 (s, OCH$_2$CH$_3$), 52.3 (s, NCH$_2$C$_6$H$_4$C(CH$_3$)$_3$), 63.9 (s, NCH$_2$CH$_2$O), 69.3 (s, NCH$_2$CH$_2$O), 83.7 (s, arom. CH of *p*-cymene), 85.0 (s, arom. CH of *p*-cymene), 85.1 (s, arom. CH of *p*-cymene), 86.6 (s, arom. CH of *p*-cymene), 98.4-150.4 (arom. *C*s), 191.5 (s, C-Ru) ppm. Elemental analysis calcd (%) for $C_{38}H_{46}RuCl_2N_2O_2$ (Mr = 734.76): C 62.12, H 6.31, N 3.81; found (%): C 62.20, H 6.40, N 3.85.

General Procedure for the *N*-Alkylation of Aniline with Alcohols: A 10 mL-Schlenk tube, under an argon atmosphere, was filled with ruthenium complex (0.025 mmol, 2.5 mol %), alcohol derivative (1.0 mmol), aniline (1.1 mmol) and ^{t}BuOK (2.5 mmol). Degassed toluene (3 mL) was then added and the reaction mixture was heated at 120 °C for 24 h. After cooling to room temperature, the reaction was cooled room temperature and filtered through a short pad of SiO_2 and the filtrate was analyzed by and GC-MS with the calibrations based on decane.

X-ray Crystallographic Data: Single crystal of complex **1a**•$CHCl_3$ suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a chloroform solution of the complex **1a**. Empirical formula = $C_{36}H_{42}RuCl_2N_2O_2.CHCl_3$, *Mr* = 826.05 g.mol^{-1}, crystal system = trigonal, space group = R-3 system, *a* = 27.383(3), *b* = 27.383(3), *c* = 26.499(3) Å,

α = 90°, β = 90°, γ = 120°, V = 17208(4) Å^3, Z = 18, d = 1.435 g.cm^{-3}, μ = 0.794 mm^{-1}, F(000) = 7632, T = 173(2) K. The crystal size (0.160 × 0.140 × 0.100 mm) was studied with a Bruker APEX2 DUO Kappa-CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by using SHELXS-2013 [30], which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all the hydrogen atoms were found by Fourier difference. The whole structure was refined with SHELXL-2013 [31] by using the full-matrix least-squares technique (use of $F2$; x, y, z, βij for C, Cl, N, O and Ru atoms, x, y, z in the riding mode for hydrogen atoms); 436 variables and 6199 observations with $I > 2.0\sigma(I)$; calcd. $w = 1/[\sigma^2(Fo^2) + (0.0801P)^2]$ in which $P = (Fo^2 + 2F_c^2)/3$. Extra solvent accessible voids were detected in **1a**•$CHCl_3$, therefore, a SQUEEZE/PLATON technique [32] was applied to remove the unidentified solvent contributions. Final results: R = 0.0526, Rw = 0.1455, Sw = 1.057 and $\Delta\rho$ < 0.961 e Å^{-3}. CCDC 1580353 contains the supplementary crystallographic data for **1a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supporting Information (see footnote on the first page of this article): Full ^{1}H NMR, ^{13}C NMR and FT-IR spectra for the of benzimidazolium bromides (**3a** and **3b**), silver(I)-NHC complexes (**4a** and **4b**) and ruthenium(II)-NHC complexes (**1a-f**) .

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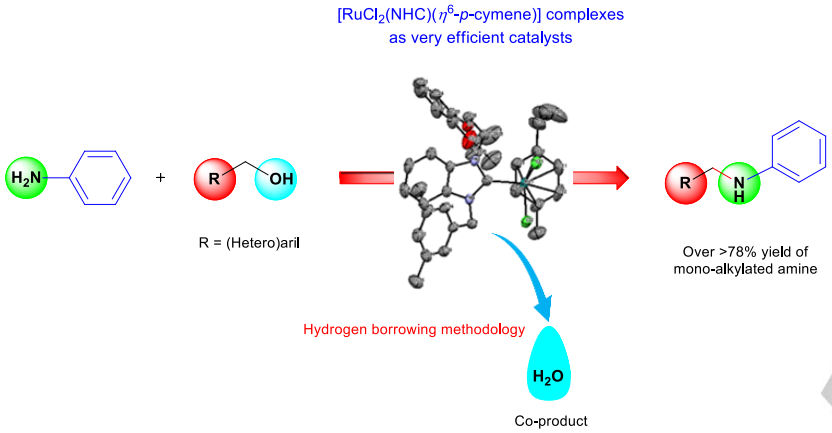

Six ruthenium(II) complexes with the general molecular formula [$RuCl_2$(NHC)(η^6-*p*-cymene)], (NHC = *N*-heterocyclic carbene) were synthesized. The obtained complexes were fully characterized by analytical and spectral methods (FT-IR, elemental analysis and ^{1}H and ^{13}C NMR). The solid-state structure of one of the ruthenium complexes {dichloro-[1-(2-(2-ethoxyphenoxy)ethyl)-3-(3,5-dimethylbenzyl)benzimidazol-2-ylidene](*p*-cymene)ruthenium(II)} has been established by single-crystal X-ray diffraction study. The catalytic activity of the all ruthenium(II) complexes have been evaluated in the *N*-alkylation of aniline using the green hydrogen borrowing methodology

Ruthenium(II)-(*p*-cymene)-*N*-Heterocyclic Carbene Complexes: Very Efficient Catalsts for The *N*-Alkylation of Aniline

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Ruthenium(II)-(*p*-cymene)-*N*-Heterocyclic Carbene Complexes for the *N*-Alkylation of Amine Using the Green Hydrogen Borrowing Methodology