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The first used half sandwich ruthenium(II) complexes bearing benzimidazole moiety for *N*-alkylation of amines with alcohols

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This paper is dedicated to Professor Irina P. Beletskaya on the occasion of her contribution to catalysis.

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ABSTRACT

Half sandwich ruthenium(II) complexes were synthesized from $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and *N*-substituted benzimidazole. All new compounds were characterized by elemental analysis, ^1H NMR, ^{13}C NMR, and IR spectroscopy. Aminoarenes were readily converted into secondary amines by the reaction at 150 °C with benzyl alcohol and in the presence of a catalytic amount of novel ruthenium complexes. All of $[RuCl_2(\eta^6\text{-}p\text{-cymene})$(*N*-substituted benzimidazole)] complexes were the most effective catalyst for *N*-alklyation reaction using borrowing hydrogen methodology.

1. Introduction

Alkylated amines are important chemicals for many uses such as synthetic intermediates, pharmaceuticals, agrochemicals, and bulk chemicals. The alkylation of amines is usually achieved by a substitution reaction with an alkyl halide, although these reactions can lead to over alkylation, and the toxicity of many alkyl halides and related alkylating agents can be problematic [1]. The *N*-alkylation of primary amines with alcohols has been recently focused as a new efficient method for the production of alkylated amines [2]. The use of alcohols as direct alkylating agents for amines is appealing since the reaction is atom economical, the alcohol is likely to be less toxic than the corresponding alkyl halide, and the only reaction byproduct is water. Due to the poor electrophilicity of simple alcohols, the direct reaction between amines and alcohols is not readily achieved. Recently, the transition metal-catalyzed dehydrative *N*-alkylation of amines and amides using alcohols as the greener alkylating reagents, namely the borrowing of hydrogen or hydrogen autotransfer methodology has become a useful way to achieve versatile amine and amide derivatives [3–8]. This strategy typically uses ruthenium or iridium as the catalyst and takes the hydrogen from the alcohol **1** to form the aldehyde **2**. This aldehyde can react with an amine to form an imine **3**, and the hydrogen is then returned to give a CN bond in product **4** (Scheme 1) [4,9–11].

Regarding the fundamental principles of a green transformation, advantageous synthetic methods avoiding mutagenic and waste-producing reagents are of extraordinary interest in both academic and industrial work [12,13]. Most common catalysts used for the alkylation of amines using alcohols are based on Ru [14,15] and Ir [16,17]. Catalysts derived from other metals, such as Au [18], Ag [19], Cu [20], Fe [21], Ni [22], Os [23], Pd [24], and Rh [25] have also been explored, and many of them showed very good activity and selectivity under moderate to higher temperatures (typically 100–200 °C). The first examples of homogeneous catalysts for the alkylation of amines by alcohols were published independently by Grigg [26] and Watanabe [27]. Many of these catalysts require rather forcing conditions, although milder conditions have been employed by Yamaguchi and co-workers with Cp^*IrCl_2 [28] and by Beller's group using $Ru_3(CO)_{12}$ with bulky phosphines [29] as well as a report on the use of $CpRuCl(PPh_3)_2$ [30]. Ruthenium complexes have been commonly used as catalysts for the *N*-alkylation of amines via a hydrogen autotransfer process, particularly $RuCl_2(PPh_3)_3$ and its derivatives [31,32]. In addition, Albretch et al. just recently described the use of ruthenium triazolylidene complexes as catalysts for oxidative coupling of alcohols and amines [33]. On the other hand,

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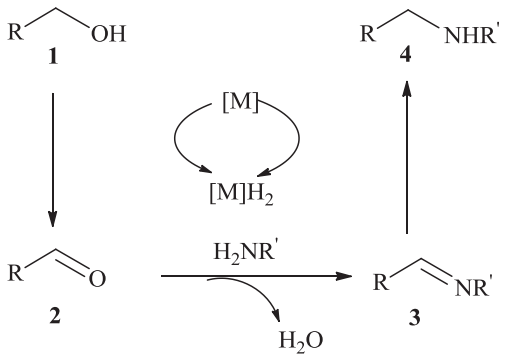


Scheme 1. Alkylation of amines with alcohols using the borrowing hydrogen strategy.

Crabtree and co-workers have also reported the use of a ruthenium pyrimidine-NHC complex as a catalyst for the *N*-alkylation of amines [17]. To the best of our knowledge, there are no previous reports of borrowing hydrogen methodology being performed by half sandwich ruthenium (II) complexes bearing benzimidazole ligand. Therefore we report the preparation of ruthenium(II) complexes having aliphatic and chloro, dichloro and methoxy bearing benzylic functionalized *N*-substituted benzimidazole ligands, and their catalytic activity in the alkylation of amines with alcohols. The first examples of the use of all new complexes as catalyst for borrowing hydrogen methodology are reported and found to be especially beneficial for the synthesis of secondary amines.

2. Results and discussion

2.1. Synthesis and characterization of ligands and their ruthenium complexes

Nitrogen containing ligands have been extensively studied in coordination chemistry, and have been shown important applications in the fields of homogeneous catalysis and organic synthesis due to the easy manipulations and high reactivities of their transition metal complexes [34]. In contrast to phosphine type ligands, the low toxicity and stability of nitrogen based ligands, such as benzimidazole derivatives, have attracted the interest of synthetic organic chemists. However, there are few reports of highly catalytic reactive complexes bearing nitrogen ligands, although there are many reports of nitrogen ligands [35–43]. We are interested in the possibility of using benzimidazole derivatives as ligands because they are structurally simple, readily available, and inexpensive, and they allow for simplistic introduction of various substituents into their structure.

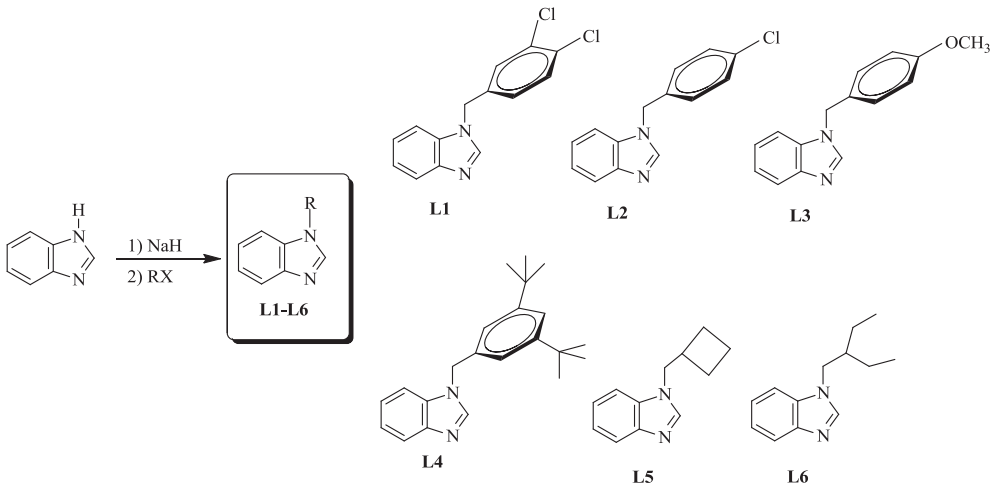
The *N*-substituted ligands (**L1**–**L6**) were prepared by the reaction of benzimidazole and base with alkyl halides in one step reaction (Scheme 2).

The synthesis and characterization of **L2** ligand have been indicated by R.W. Hartmann in 2011 [43]. All new ligands were isolated as colorless and air-stable solids. They were characterized by ^{1}H NMR, ^{13}C NMR, IR, elemental analysis techniques which support the proposed structures. The analytical data are in good agreement with the compositions proposed for all the ligands are presented in Table 1.

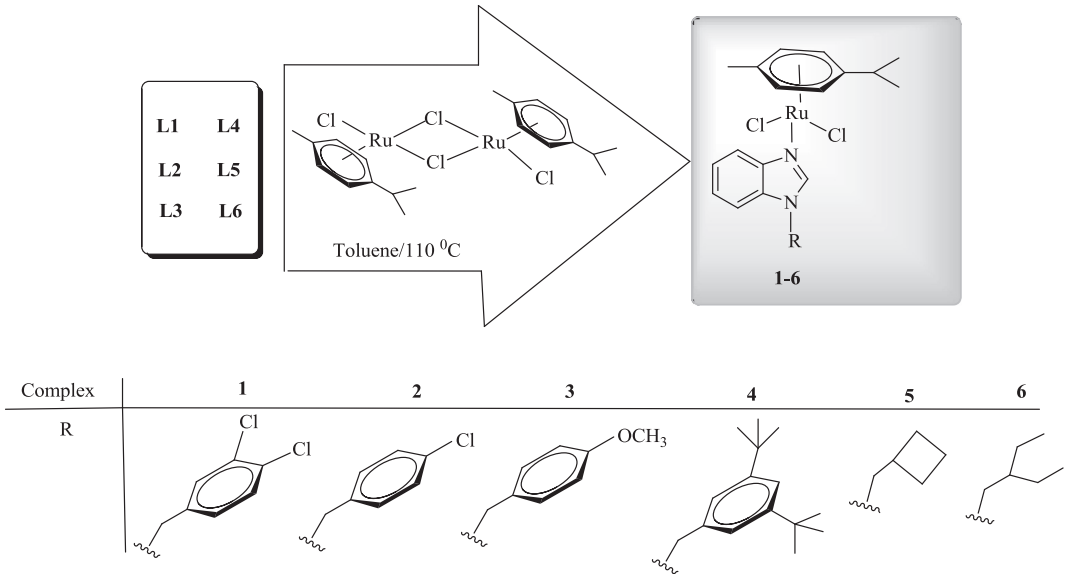
Coordination was immediate, as a change of color from red to orange. All the complexes were isolated as air-stable, non-hygroscopic solids and soluble in dimethylformamide, dimethylsulfoxide and halogenated solvents such as chloroform, dichloromethane but insoluble in petroleum ether, diethyl ether, and *n*-hexane and do not show any signs of decomposition in solution upon exposure to air for days. New benzimidazole ligands and [$RuCl_2(\eta^6$-*p*-cymene)(*N*-substituted benzimidazole)] complexes have been two important advantage. The first, all compounds can be synthesized in a single step, latter the products both in solution and in the solid state is stable structure. The ^{1}H and ^{13}C NMR of **L1**–**L6** showed that the NCHN resonances occurred between 7.93–8.22 ppm and 143.4–144.9 ppm, respectively. The values of complexes (**1**–**6**) also showed that the NCHN resonances occurred between 8.41–8.45 ppm and 144.4–145.0 ppm, respectively. The ^{1}H NMR values showed that the C2–H signals shifted to low fieldin the ruthenium complexes as compared to corresponding ligand due to an electron withdrawing effect of the metal center. The presence of the –C=N– group in the complexes was verified by the υ(C=N) vibrations between 1507 and 1522 cm^{-1}. The NMR and IR values are similar to those found for other *N*-substituted benzimidazole and [$RuCl_2(\eta^6$-*p*-cymene)(*N*-substituted benzimidazole)] complexes [39–43]. The analytical data are in good agreement with the general molecular formula proposed for all the complexes (Table 1).

2.2. Catalytic application of ruthenium complexes for N-alkylation reaction

An environmentally benign approach is the *N*-alkylation of amines with readily available alcohols using borrowing hydrogen methodology [3–11]. The *N*-alkylation has been mainly studied in



Scheme 2. Synthesis of *N*-substituted benzimidazole ligands.



Scheme 3. Synthesis of half sandwich ruthenium (II) complexes.

the presence of homogeneous metal catalysts [27,44–46]. But to the best of our knowledge, there are no previous reports of borrowing hydrogen methodology being performed by half sandwich ruthenium complex bearing benzimidazole moiety. This prompted us to test the catalytic activities of new ruthenium complexes for *N*-alkylation of amines with alcohols. Initially, we studied the reaction of aniline with benzyl alcohol as a model reaction. The reaction was carried out using aniline (0.55 mmol) and benzyl alcohol (0.5 mmol) in toluene in the presence of [$RuCl_2$(*p*-cymene)(**L1**)] (**1**) as catalyst (1.0 mol%) and base (0.5 mmol) at 150 °C for 15 h. The results are summarized in Table 2.

When the reaction was carried out without a base, neither amine nor imine was formed (Table 2, entry 1). The reaction was considerably accelerated by addition of a base. When the reaction was carried out in the presence of ^{t}KOBu, *N*-benzylaniline was formed in an excellent yield (>99%), while moderate yield (67%) was observed with KOH base (Table 2, entries 2 and 3). On the other hand, desired product was not observed with Cs_2CO_3 and NaOH bases (Table 2, entries 4 and 5). After optimization of the reaction conditions, the *N*-alkylation reactions of amines with benzyl alcohol and *p*-methylbenzyl alcohol were tested (Table 3).

It is interesting to explore the byproducts of the *N*-alkylation reactions. By tracing the reactions by using GCMS, imine was also observed as the major or minor byproduct in all of the reactions between benzyl alcohol and primary amines. Surprisingly, the reaction under similar conditions using potassium hydroxide at 100 °C for 24 h gave only imine in good yield (Table 3, entry 2). With higher temperatures (150 °C) amine formation was observed instead of the expected imine (Table 3, entry 4). However in similar reaction condition there was no formation of any product at 5 h (Table 3, entry 5). Corresponding imine was obtained as a minor product when we used equal amounts of aniline (0.5 mmol) and benzyl alcohol (0.5 mmol) (Table 3, entries 6–11). The temperature of the reaction was found to have a strong impact on the reaction rate. The temperature could be lowered, but in this case the selectivity decreases. (130 °C, 79% amine, Table 3, entry 12 compared 150 °C, >99% amine, Table 3, entry 13). All catalysts have been good activity for the synthesis of *N*-benzyl amine (Table 3, entries 13–18). As previously reported for related Ru catalysts such as pyrimidine–NHC–Ru [17], the *N*-alkylation of benzyl alcohol and aniline was retarded at 45h-110 °C. In the present catalytic system using [$RuCl_2$(η^6-*p*-cymene)(*N*-substituted benzimidazole)] complexes was particularly effective for the same reaction at 15 h-150 °C. Complex **1** was chosen for further optimization studies (catalyst loading and temperature) due to its high reactivity. With the best catalyst full conversion was obtained 10 h and the lower the catalyst loading (0.25 mol%) (Table 3 entries 19,28 and 20,29,30 respectively). The reaction of aniline with *p*-methylbenzyl alcohol successfully converted corresponding secondary amine (Table 3 entries 22,24,26 and 28–30). The reaction of 2,4-dimethylaniline with benzyl alcohol/*p*-methylbenzyl alcohol transformed into the corresponding *N*-benzyl amines (Table 3 entries 31,32). As shown in Table 3 electronic and steric effects of benzimidazole substituents was not caused remarkable difference on the catalytic performance.

Table 1
Selected analytical data for the ligand (**L1**–**L6**) and ruthenium complexes (**1**–**6**).

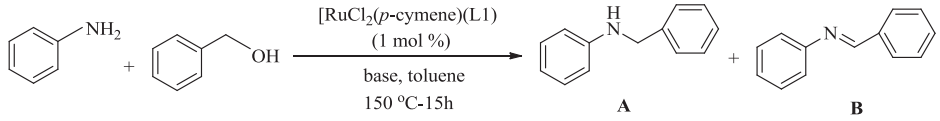
Compound	Isolated yield (%)	M.p. (°C)	$\upsilon_{(C=N)}$ (cm^{-1})	^{13}C NMR C(2) (ppm)	^{1}H NMR H(2) (ppm)
L1	92	128–129	1493	143.4	8.15
L2	63	68–69	1490	144.0	7.94 [43]
L3	92	64–65	1492	143.9	7.94
L4	88	137–138	1450	143.7	7.97
L5	89	63–64	1493	143.5	7.93
L6	81	44–45	1456	144.9	8.22
1	69	232–233	1507	144.9	8.42
2	72	228–229	1509	144.9	8.45
3	85	222–223	1512	144.8	8.41
4	78	221–222	1516	144.9	8.55
5	68	235–236	1522	144.4	8.45
6	75	214–215	1513	145.0	8.45

Reaction of 1:2 ratio of [Ru(*p*-cymene)Cl_2]$_2$ with **L** in toluene at 110 °C for 5 h afforded half sandwich ruthenium (II) complexes (**1**–**6**) in good yield (Scheme 3).

3. Conclusion

In conclusion, inexpensive and easily prepared half sandwich ruthenium (II) complexes bearing benzimidazole moiety have been shown to be an active, stable, versatile, and highly selective catalyst for the selective monoalkylation of aromatic amines. The protocol has been applied for the first time successfully by this type complexes. In future *N*-alkylation reaction can be improved for secondary amine and different alcohol.

Table 2
Effects of bases on *N*-alkylation of aniline with benzyl alcohol catalyzed by **1**.



Entry	Base	Yield (%)	
		A	B
1	No	–	–
2	^{t}KOBu	>99	
3	KOH	67	33
4	Cs_2CO_3	–	–
5	NaOH	–	–

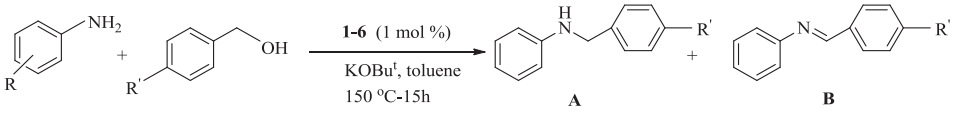
Reaction conditions: Aniline (0.55 mmol), benzyl alcohol (0.5 mmol), cat. (1.0 mol%), base (0.5 mmol), toluene (2 mL), 150 °C-15 h.

4. Experimental

4.1. General procedures

All reactions for the preparation of *N*-substituted benzimidazole as ligand and their ruthenium complexes were carried out under argon in flame-dried glassware using standard Schlenk techniques. Chemicals were obtained from Sigma Aldrich and Fluka. Melting points were determined in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a Perkin Elmer Spectrum 100. ^1H and ^{13}C NMR

Table 3
N-Alkylation of anilines with benzyl alcohol derivatives in the presence of [$RuCl_2$(*p*-cymene)(**L1**–**L6**)].



Entry	Ru complex	Temp./time/base	R	R'	Yield (%)	
					A	B
1	1	100 °C/24 h/^{t}KOBu	H	H	50	50
2	1	100 °C/24 h/KOH	H	H	–	100
3	4	100 °C/24 h/KOH	H	H	29	71
4	1	150 °C/15 h/KOH	H	H	67	33
5	1	150 °C/5 h/^{t}KOBu	H	H	–	–
6[a]	1	150 °C/15 h/^{t}KOBu	H	H	98	2
7[a]	2	150 °C/15 h/^{t}KOBu	H	H	83	17
8[a]	5	150 °C/15 h/^{t}KOBu	H	H	82	18
9[a]	3	150 °C/15 h/^{t}KOBu	H	H	94	6
10[a]	6	150 °C/15 h/^{t}KOBu	H	H	79	21
11[a]	4	150 °C/15 h/^{t}KOBu	H	H	92	8
12	1	130 °C/15 h/^{t}KOBu	H	H	79	21
13	1	150 °C/15 h/^{t}KOBu	H	H	>99	
14	2	150 °C/15 h/^{t}KOBu	H	H	>99	
15	3	150 °C/15 h/^{t}KOBu	H	H	>99	
16	4	150 °C/15 h/^{t}KOBu	H	H	>99	
17	5	150 °C/15 h/^{t}KOBu	H	H	>99	
18	6	150 °C/15 h/^{t}KOBu	H	H	>99	
19	1	150 °C/10 h/^{t}KOBu	H	H	>99	
20[b]	1	150 °C/15 h/^{t}KOBu	H	H	>99	
21[c]	1	150 °C/15 h/^{t}KOBu	H	H	95	25
22	1	150 °C/15 h/^{t}KOBu	H	*p*-CH_3	>99	
23	2	150 °C/15 h/^{t}KOBu	H	*p*-CH_3	75	25
24	3	150 °C/15 h/^{t}KOBu	H	*p*-CH_3	>99	
25	4	150 °C/15 h/^{t}KOBu	H	*p*-CH_3	97	3
26	5	150 °C/15 h/^{t}KOBu	H	*p*-CH_3	>99	
27	6	150 °C/15 h/^{t}KOBu	H	*p*-CH_3	65	35
28	1	150 °C/10 h/^{t}KOBu	H	*p*-CH_3	>99	
29[b]	1	150 °C/15 h/^{t}KOBu	H	*p*-CH_3	>99	
30[c]	1	150 °C/15 h/^{t}KOBu	H	*p*-CH_3	>99	
31	1	150 °C/15 h/^{t}KOBu	2,4-(CH_3)	H	83	17
32	1	150 °C/15 h/^{t}KOBu	2,4-(CH_3)	*p*-CH_3	72	28

Reaction conditions: Aniline (0.55 mmol), benzyl alcohol (0.5 mmol), cat. (1.0 mol%), base (0.5 mmol), toluene (2 mL), 150 °C-15 h.
[a] Aniline (0.5 mmol).
[b] Cat. (0.5 mol%).
[c] Cat. (0.25 mol%).

spectra were recorded with a Varian AS 400 Merkur spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. Coupling constants (*J* values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, hept = heptet, and m = multiplet signal. All catalytic reactions were monitored on an Agilent 6890N GC system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Column chromatography was performed using silica gel 60 (70–230 mesh). Solvent ratios are given as v/v.

4.2. Synthesis and characterization of 1-alkylbenzimidazole ligand (**L1**–**L6**)

4.2.1. General procedure for the preparation of the 1-alkylbenzimidazole

Benzimidazole (10 mol) was added to a solution of NaH (10 mol) in dry THF (30 mL), the mixture was stirred for 1 h at room temperature, and the corresponding alkyl halides (10.1 mol) was added dropwise and heated for 8 h. The solvent was removed in vacuum, after that dichloromethane (50 mL) was added in the Schlenk tube. The mixture was filtered and then the salt was separated from solution. The solution was concentrated and diethyl ether was added. The colorless product was obtained as a crystal.

4.2.1.1. N-(3,4-Dichlorobenzyl)benzimidazole, ***L1***. Yield: 2.55 g (92%). FT-IR $\upsilon_{(CN)}$: 1493 cm^{-1}, m.p.: 128–129 °C. Anal. Calc. for $C_{14}H_{10}N_2Cl_2$: C, 60.67; H, 3.64; N, 10.11. Found: C, 60.62; H, 3.66; N: 10.18%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 8.15 (s, 1H, NC*H*N), 7.90–7.85 (m, 1H, NC_6H_4N), 7.48–7.25 (m, 5H, NC_6H_4N and $CH_2C_6H_3Cl_2$-3,4), 7.03–6.99 (m, 1H, NC_6H_4N), 5.37 (s, 2H, $CH_2C_6H_3Cl_2$-3,4). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 143.4 (N*C*HN), 142.9, 135.6, 133.5, 133.4, 132.6, 131.1, 128.9, 126.2, 123.6, 122.8, 120.5109.9 (NC_6H_4N and $CH_2C_6H_3Cl_2$-3,4), 47.8 ($CH_2C_6H_3Cl_2$-3,4).

4.2.1.2. N-(4-Chlorobenzyl)benzimidazole, ***L2***. Synthesis and characterization data has been given by R.W. Hartmann [43].

4.2.1.3. N-(4-Methoxybenzyl)benzimidazole, ***L3***. Yield: 2.19 g (92%). FT-IR $\upsilon_{(CN)}$: 1492 cm^{-1}, m.p.: 64–65 °C. Anal. Calc. for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.65; H, 5.90; N: 11.77%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 7.94 (s, 1H, NC*H*N), 7.87–7.82 (m, 1H, NC_6H_4N), 7.35–7.23 (m, 3H, NC_6H_4N), 7.16 (d, 2H, *J* = 11.1 Hz, $CH_2C_6H_4(OCH_3)$-4), 6.89 (d, 2H, *J* = 11.7 Hz, $CH_2C_6H_4(OCH_3)$-4), 5.30 (s, 2H, $CH_2C_6H_4(OCH_3)$-4), 3.80 (s, 3H, $CH_2C_6H_4(OCH_3)$-4). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 143.9 (N*C*HN), 159.6, 143.1, 133.9, 128.7, 127.4, 123.0, 122.2, 120.4, 114.4, and 110.1(NC_6H_4N and $CH_2C_6H_4(OCH_3)$-4), 55.3 ($CH_2C_6H_4(OCH_3)$-4), 48.5 ($CH_2C_6H_4(OCH_3)$-4).

4.2.1.4. N-(3,5-Ditert-butylbenzyl)benzimidazole, ***L4***. Yield: 2.82 g (88%). FT-IR $\upsilon_{(CN)}$: 1450 cm^{-1}, m.p.: 137–138 °C. Anal. Calc. for $C_{22}H_{28}N_2$: C, 82.45; H, 8.81; N, 8.74. Found: C, 82.48; H, 8.83; N: 8.72%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 7.97 (s, 1H, NC*H*N), 7.87–7.84 (m, 1H, NC_6H_4N), 7.41–7.28 (m, 4H, NC_6H_4N and $CH_2C_6H_3(C(CH_3)_3)_2$-3,5), 6.88–6.74 (m, 2H, $CH_2C_6H_3(C(CH_3)_3)_2$-3,5), 5.36 (s, 2H, $CH_2C_6H_3(C(CH_3)_3)_2$-3,5), 1.30 (s, 18H, $CH_2C_6H_3(C(CH_3)_3)_2$)-3,5). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 143.7 (N*C*HN), 151.8, 143.0, 134.3, 134.1, 126.9, 123.0, 122.5, 122.4, 122.3, 121.7, 120.3, and 110.1(NC_6H_4N and $CH_2C_6H_3(C(CH_3)_3)_2$)-3,5), 49.5 ($CH_2C_6H_3(C(CH_3)_3)_2$)-3,5), 34.9 ($CH_2C_6H_3(C(CH_3)_3)_2$)-3,5), 31.4 ($CH_2C_6H_3(C(CH_3)_3)_2$)-3,5).

4.2.1.5. N-(Methylcyclobutane)benzimidazole, ***L5***. Yield: 1.66 g (89%). FT-IR $\upsilon_{(CN)}$: 1493 cm^{-1}, m.p.: 63–64 °C. Anal. Calc. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.35; H, 7.54; N: 15.01%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 7.93 (s, 1H, NC*H*N), 7.85–7.79 (m, 1H, NC_6H_4N), 7.44–7.39 (m, 1H, NC_6H_4N), 7.35–7.26 (m, 2H, NC_6H_4N), 4.17 (d, 2H, *J* = 7.2 Hz, $CH_2CH(CH_2)_2CH_2$), 2.89 (hept., 1H, *J* = 7.5 Hz, $CH_2CH(CH_2)_2CH_2$), 2.13–2.03 (m, 2H, $CH_2CH(CH_2)_2CH_2$), 2.00–1.76 (m, 4H, $CH_2CH(CH_2)_2CH_2$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 144.3 (NCHN), 143.9, 134.5, 122.7, 121.8, 119.9, 110.9 (NC_6H_4N), 49.4 ($CH_2CH(CH_2)_2CH_2$), 35.4 ($CH_2CH(CH_2)_2CH_2$), 25.7 ($CH_2CH(CH_2)_2CH_2$), 18.0 ($CH_2CH(CH_2)_2CH_2$).

4.2.1.6. N-(2-Ethylbutane)benzimidazole, ***L6***. Yield: 1.64 g (81%). FT-IR $\upsilon_{(CN)}$: 1456 cm^{-1}, m.p.: 44–45 °C. Anal. Calc. for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.15; H, 8.94; N: 13.81%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 8.22 (s, 1H, NC*H*N), 7.66–7.55 (m, 2H, NC_6H_4N), 7.27–7.17 (m, 2H, NC_6H_4N), 4.13 (d, 2H, *J* = 7.25 Hz, $CH_2CH(CH_2CH_3)_2$, 1.83(hept., 1H, *J* = 6.75 Hz, $CH_2CH(CH_2CH_3)_2$), 1.25 (p, 4H, *J* = 7.5 Hz, $CH_2CH(CH_2CH_3)_2$), 0.86 (t, 6H, *J* = 6.9 Hz, $CH_2CH(CH_2CH_3)_2$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 144.9 (NCHN), 143.9, 134.5, 122.7, 121.8, 119.9, 110.9 (NC_6H_4N), 47.9 ($CH_2CH(CH_2CH_3)_2$), 39.2 ($CH_2CH(CH_2CH_3)_2$), 23.2 ($CH_2CH(CH_2CH_3)_2$), 10.8 ($CH_2CH(CH_2CH_3)_2$).

4.3. Synthesis and characterization of the half sandwich ruthenium(II) complexes (**1**–**6**)

4.3.1. General procedure for the preparation of the half sandwich ruthenium(II) complexes

A solution of *N*-alkylbenzimidazole (1.0 mol) and [$RuCl_2$(*p*-cymene)]$_2$ (0.5 mol) in 10 mL toluene was heated under reflux for 5 h. Upon cooling to room temperature, orange crystals of **1**–**6** were obtained. The crystals were filtered off, washed with diethyl ether (3 × 15 mL) and dried under vacuum.

4.3.1.1. Dichloro-(N-(3,4-dichlorobenzyl)benzimidazole)(p-cymene) ruthenium(II), ***1***. Yield: 0.40 g (69%). FT-IR $\upsilon_{(CN)}$: 1507 cm^{-1}, m.p.: 232–233 °C. Anal. Calc. for $C_{24}H_{24}Cl_4N_2Ru$: C, 49.41; H, 4.15; N, 4.80. Found: C, 49.45; H, 4.12; N:4.76%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 8.42 (s, 1H, NC*H*N), 8.03 (d, 1H, *J* = 8.4 Hz, NC_6H_4N), 7.36–7.14 (m, 6H, NC_6H_4N and $CH_2C_6H_3Cl_2$-3,4), 5.55 (d, 2H, *J* = 6.0 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 5.42 (d, 2H, *J* = 6.0 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 4.97 (s, 2H, $CH_2C_6H_3Cl_2$-3,4), 2.77 (hept., 1H, *J* = 6.0 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 2.11 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-4), 1.24 (d, 6H, *J* = 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-4). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 144.9 (NCHN), 142.3, 135.4, 133.2, 133.0, 132.6, 131.0, 128.8, 127.2, 124.8, 123.4, 111.6 (NC_6H_4N and $CH_2C_6H_3Cl_2$-3,4), 102.4, 98.0, 83.1, 81.1 (($CH_3)_2CHC_6H_4CH_3$-4), 48.2 ($CH_2C_6H_3Cl_2$-3,4), 30.7 (($CH_3)_2CHC_6H_4CH_3$-4), 22.3 (($CH_3)_2CHC_6H_4CH_3$-4), 18.5 (($CH_3)_2CHC_6H_4CH_3$-4).

4.3.1.2. Dichloro-(N-(4-chlorobenzyl)benzimidazole)-(p-cymene) ruthenium(II), ***2***. Yield: 0.39 g (72%). FT-IR $\upsilon_{(CN)}$: 1509 cm^{-1}, m.p.: 228–229 °C. Anal. Calc. for $C_{24}H_{25}Cl_3N_2Ru$: C, 52.52; H, 4.59; N, 5.10. Found: C, 52.48; H, 4.62; N: 5.15%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 8.45 (s, 1H, NC*H*N), 8.03 (d, 1H, *J* = 7.8 Hz NC_6H_4N), 7.38–7.25 (m, 3H, NC_6H_4N), 7.26 and 7.12 (d, 4H, *J* = 8.4 Hz, $CH_2C_6H_4Cl$-4), 5.55 (d, 2H, *J* = 6.0 Hz $(CH_3)_2CHC_6H_4CH_3$-4), 5.40 (d, 2H, *J* = 6.0 Hz $(CH_3)_2CHC_6H_4CH_3$-4), 5.08 (s, 2H, $CH_2C_6H_4Cl$-4), 2.81 (hep. 1H, *J* = 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 2.1 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-4), 1.24 (d, 6H, *J* = 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-4). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 144.9 (NC*H*N), 142.5, 134.4, 133.5, 133.4, 129.2, 128.8, 124.5, 123.6, 120.5, 111.4 (NC_6H_4N and $CH_2C_6H_4Cl$-4), 102.5, 97.8, 83.0, 81.1 (($CH_3)_2CHC_6H_4CH_3$-4), 48.7 ($CH_2C_6H_4Cl$-4),

30.7 ($(CH_3)_2CHC_6H_4CH_3$-4), 22.3 ($(CH_3)_2CHC_6H_4CH_3$-4), 18.5 ($(CH_3)_2CHC_6H_4CH_3$-4).

4.3.1.3. Dichloro-(N-(4-methoxybenzyl)benzimidazole)-(p-cymene) ruthenium(II), ***3***. Yield: 0.46 g (85%). FT-IR $\upsilon_{(CN)}$: 1512 cm^{-1}, m.p.: 222–223 °C. Anal. Calc. for $C_{25}H_{28}Cl_2N_2ORu$: C, 55.15; H, 5.18; N, 5.14. Found: C, 55.09; H, 5.22; N: 5.17%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 8.41 (s, 1H, NC*H*N), 8.02 (d, 1H, J = 7.5 Hz, NC_6H_4N), 7.33–7.28 (m, 3H, NC_6H_4N), 7.14 (d, 2H, J = 8.1 Hz, $CH_2C_6H_4(OCH_3)$-4), 6.82 (d, 2H, J = 8.1 Hz, $CH_2C_6H_4(OCH_3)$-4), 5.50 (d, 2H, J = 5.4 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 5.37 (d, 2H, J = 5.7 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 5.10 (s, 2H, $CH_2C_6H_4(OCH_3)$-4), 3.76 (s, 3H, $CH_2C_6H_4(OCH_3)$-4), 2.77 (hept. 1H, J = 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 2.07 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-4), 1.21 (d, 6H, J = 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-4). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 144.8 (NCHN), 159.6, 144.8, 142.6, 133.6, 129.1, 126.7, 124.2, 123.5, 120.4, 114.4, and 111.6 (NC_6H_4N and $CH_2C_6H_4(OCH_3)$-4), 102.3, 97.8, 83.0 and 81.1 ($(CH_3)_2CHC_6H_4CH_3$-4), 55.4 ($CH_2C_6H_4(OCH_3)$-4), 49.2 ($CH_2C_6H_4(OCH_3)$-4), 30.6 ($(CH_3)_2CHC_6H_4CH_3$-4), 22.3 ($(CH_3)_2CHC_6H_4CH_3$-4), 18.5 ($(CH_3)_2CHC_6H_4CH_3$-4).

4.3.1.4. Dichloro-(N-(3,5-diter-butylbenzyl)benzimidazole)(p-cymene)ruthenium(II), ***4***. Yield: 0.49 g (78%). FT-IR $\upsilon_{(CN)}$: 1516 cm^{-1}, m.p.: 221–222 °C. Anal. Calc. for $C_{32}H_{42}Cl_2N_2Ru$: C, 61.33; H, 6.76; N, 4.47. Found: C, 61.37; H, 6.70; N: 4.48%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 8.55 (s, 1H, NC*H*N), 8.08 (d, 1H, J = 6.9 Hz, NC_6H_4N), 7.43–7.28 (m, 4H, NC_6H_4N and $CH_2C_6H_3(C(CH_3)_3)_2$-3,5), 7.11 and 7.10 (s, 2H, $CH_2C_6H_3(C(CH_3)_3)_2$-3,5), 5.54 (d, 2H, J = 6.0 Hz $(CH_3)_2CHC_6H_4CH_3$-4), 5.39 (d, 2H, J = 6.0 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 5.29 (s, 2H $CH_2C_6H_3(C(CH_3)_3)_2$-3,5), 2.82 (hept. 1H, J = 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 2.11 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-4), 1.30 (s, 18H, $CH_2C_6H_3$ ($C(CH_3)_3)_2$)-3,5), 1.22 (d, 6H, J = 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-4). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 144.9 (NC*H*N), 151.9, 142.7, 134.0, 133.5, 124.1, 123.6, 122.8, 121.9, 120.7, 111.1 (NC_6H_4N and $CH_2C_6H_3(C(CH_3)_3)_2$-3,5), 102.3, 97.8, 83.2, 81.0 ($(CH_3)_2CHC_6H_4CH_3$-4), 50.4 ($CH_2C_6H_3(C(CH_3)_3)_2$-3,5), 34.9 ($CH_2C_6H_3(C(CH_3)_3)_2$-3,5) 31.4 ($CH_2C_6H_3(C(CH_3)_3)_2$)-3,5), 30.7 ($(CH_3)_2CHC_6H_4CH_3$-4), 22.3 ($(CH_3)_2CHC_6H_4CH_3$-4), 18.5 ($(CH_3)_2CHC_6H_4CH_3$-4).

4.3.1.5. Dichloro-(N-methylcyclobutane)benzimidazole-(p-cymene) ruthenium(II), ***5***. Yield: 0.33 g (68%). FT-IR $\upsilon_{(CN)}$: 1522 cm^{-1}, m.p.: 235–236 °C. Anal. Calc. for $C_{22}H_{28}Cl_2N_2Ru$: C, 53.66; H, 5.73; N, 5.69. Found: C, 53.70; H, 5.69; N: 5.71%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 8.45 (s, 1H, NC*H*N), 8.04 (d, 1H, J = 8.4 Hz, NC_6HN), 7.41–7.34 (m, 3H, NC_6H_4N), 5.55 (d, 2H, J = 5.7 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 5.40 (d, 2H, J = 5.7 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 4.11 (d, 2H, J = 7.5 Hz, $CH_2CH(CH_2)_2CH_2$), 2.87 (hept. 1H, J = 6.6 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 2.15 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-4), 2.05–1.71 (m, 6H, $CH_2CH(CH_2)_2CH_2$), 1.26 (d, 6H, J = 6.9 ($(CH_3)_2CHC_6H_4CH_3$-4). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 144.4 (NCHN), 142.5, 133.9, 124.0, 123.5, 120.6, 110.7 (NC_6H_4N), 102.5, 97.8, 82.9, 81.2 ($(CH_3)_2CHC_6H_4CH_3$-4), 50.8 ($CH_2CH(CH_2)_2CH_2$), 34.9 ($CH_2CH(CH_2)_2CH_2$), 30.7 ($(CH_3)_2CHC_6H_4CH_3$-4), 26.1 ($CH_2CH(CH_2)_2CH_2$), 22.3 ($(CH_3)_2CHC_6H_4CH_3$-4), 18.5 ($(CH_3)_2CHC_6H_4CH_3$-4), 18.0 ($CH_2CH(CH_2)_2CH_2$).

4.3.1.6. Dichloro-(2-ethylbutane)benzimidazole-(p-cymene)ruthenium(II), ***6***. Yield: 0.38 g (75%). FT-IR $\upsilon_{(CN)}$: 1513 cm^{-1}, m.p.: 214–215 °C. Anal. Calc. for $C_{23}H_{32}Cl_2N_2Ru$: C, 54.33; H, 6.34; N, 5.51. Found: C, 54.29; H, 6.35; N: 5.55%. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 8.45 (s, 1H, NC*H*N), 8.05–6.74 (m, 4H, NC_6H_4N), 5.56 (d, 2H, J = 5.4 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 5.42 (d, 2H, J = 5.4 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 4.01 (d, 2H, J = 6.9 Hz, $CH_2CH(CH_2CH_3)_2$), 2.85 (hept., 1H, J = 6.9 Hz, $(CH_3)_2CHC_6H_4CH_3$-4), 2.16 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-4), 1.86 (m, 1H, $CH_2CH(CH_2CH_3)_2$), 1.36–1.33 (m, 4H, $CH_2CH(CH_2CH_3)_2$), 1.27 (d, 6H, J = 6.9 Hz, ($(CH_3)_2CHC_6H_4CH_3$-4), 0.94 (t, 6H, J = 7.2 Hz, $CH_2CH(CH_2CH_3)_2$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 145.0 (NCHN), 142.6, 134.0, 124.0, 123.5, 120.7, 110.8 (NC_6H_4N), 49.3 ($CH_2CH(CH_2CH_3)_2$), 30.7 ($(CH_3)_2CHC_6H_4CH_3$-4), 40.8 ($CH_2CH(CH_2CH_3)_2$), 23.2 ($CH_2CH(CH_2CH_3)_2$), 22.3 ($(CH_3)_2CHC_6H_4CH_3$-4), 18.5 ($(CH_3)_2CHC_6H_4CH_3$-4), 10.5 ($CH_2CH(CH_2CH_3)_2$).

4.4. General procedure for the N-alkylation of aniline and alcohol

Under an inert atmosphere, a mixture containing the complexes [$RuCl_2$(*N*-alkylbenzimidazole)(*p*-cymene)] (**1**–**6**) (1 mol%), ^{t}KOBu (0.5 mmol), aniline (0.55 mmol), and alcohol (0.5 mmol) was heated at 100–150 °C in toluene (2 mL) for 5–24 h. After completion, the mixture was cooled, filtered and concentrated. The products were purified by column chromatography to give the *N*-alkylation products in good yields.

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