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Research paper

Half-sandwich ruthenium-carbene catalysts: Synthesis, characterization, and catalytic application in the *N*-alkylation of amines with alcohols

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ABSTRACT

In this study, the synthesis and characterization of new half-sandwich ruthenium complexes containing oxygen functionalised *N*-aryl and *N*-alkyl benzimidazol-2-ylidene ligands have been reported. All ruthenium complexes were tested as catalysts for a wide range of substrates in the *N*-alkylation of secondary cyclic amines such as pyrrolidine and piperidine, and 4-methylaniline which was a primary aromatic amine with alcohols by hydrogen-borrowing process. The catalytic reactions were performed with 1 mol% catalyst loading at 120 °C, 16 h under solvent-free conditions. All ruthenium complexes showed excellent catalytic activity, and *N*-alkylated products were obtained selectively.

1. Introduction

The synthesis of higher-order amines such as secondary and tertiary amines which are more commercially valuable by *N*-alkylation of primary amines is one of the most fundamental and important reactions in organic synthesis [1,2]. The most preferred method for *N*-alkylation of amines is the coupling of amines with alkyl halides in the presence of a stoichiometric amount of base. However, this method can be highly problematic because of the toxic nature of many alkylating agents and the formation of undesirable salts as by-products. Therefore, the development of improved synthetic methodologies for the preparation of the alkylated amines continue to be of significant interest to organic chemists. *N*-Alkylation of amines with readily available and cheap alcohols by *via* hydrogen auto-transfer, also known as hydrogen-borrowing process is an alternative approach that minimizes the generation of wasteful products [3,4]. This process involves the conversion of alcohols to aldehydes or ketones as temporary intermediates *via* an oxidative hydrogen elimination. The *in situ* generated carbonyl groups are highly reactive to nucleophiles such as amines. After reduction of the resulting imine, the expected *N*-alkylated amines are obtained and only water is generated as by-product. Nowadays, this approach has significantly been using as an effective method for making N−C(sp^3) bonds, which are frequently found in biologically active compounds and functional materials [5]. This approach environmentally more attractive because of it is more atom economical and less hazardous process than the use of conventional alkylating agents.

The first examples of homogeneous metal-catalyzed *N*-alkylation of aliphatic and aromatic amines were reported independently by Grigg [6] and Watanabe [7] using rhodium- and ruthenium-phosphine catalysts in the early 1980s. Murahashi [8] also reported an alternative ruthenium-phosphine catalyst for alkylation of aliphatic amines. Then, great contributions have been made for this approach by Zhao [9], Williams [10], Beller [11], Milstein [12] and Fujita [13]. In most of the these reports, alkylation of amines with alcohols have been generally catalyzed by ruthenium and iridium complexes [14], and these complexes are shown to be highly effective for this reaction. Recently, important progress in hydrogen-borrowing processes were also achieved based on other noble metals such as gold [15], silver [16], rhodium [17] and palladium [18] as well as non-noble metals such as iron [19], copper [20], nickel [21] and etc. [22].

N-Heterocyclic carbenes (NHCs) represent a prominent class of ligands, widely used in organometallic and inorganic chemistry [23]. The strong σ-donating but poor π-accepting ability of NHC ligands lead to the formation of many stable metal-NHC complexes. Due to activity and stability of metal-NHC complexes, they have been widely used in organometallic chemistry and catalysis as an ideal alternative to well-known phosphine ligands for the synthesis of homogeneous catalysts. Many types of *N*-alkyl, *N*-aryl and *N*-benzyl (benz)imidazol-2-ylidene ligands have been used in transition-metal catalysis [24] and medical applications [25], and many research groups have provided a large

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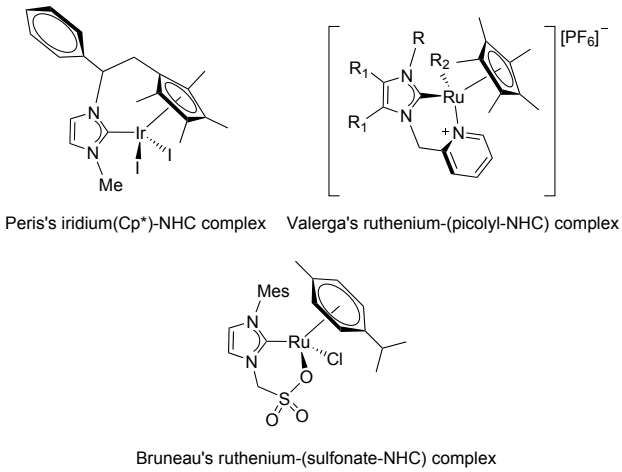


Fig. 1. Well-known iridium- and ruthenium-catalysts for the alkylation of amines.

number of NHC-based complexes. In recent years, ruthenium- and iridium-NHC complexes have been reported to be active catalysts for the alkylation of amines with alcohols. In particular, ruthenium(arene)- and iridium(Cp*)-NHC complexes (Cp* = pentamethylcyclopentadienyl) were used in these reactions. As an early example, iridium(Cp*)-type NHC complexes have been reported for the *N*-alkylation of aniline by Peris et al. [26]. Later, Crabtree and co-workers have described the use of NHC complexes of iridium and ruthenium containing chelating pyrimidine ligand as effective catalysts for the alkylation of amines and secondary alcohols [27]. Valerga and co-workers reported the *N*-alkylation of both aromatic and non-aromatic amines catalysed by ruthenium-picolyl-NHC complexes [28]. Bruneau and co-workers have shown that the half-sandwich ruthenium complexes bearing a chelating sulfonate-NHC ligand were efficient catalysts for the *N*-alkylation of aniline and cyclic secondary amines with benzylic and aliphatic alcohols, and the regioselective *C*3-alkylation of *N*-protected cyclic secondary amines with aldehydes [29], (Fig. 1). More recently, ruthenium (arene) complexes (arene = η^6-*p*-cymene) containing NHC ligand have been used as catalyst to obtain tertiary amines from cyclic secondary amines [30].

Up to now, many examples of transiton-metal-catalyzed synthesis of higher amines have been reported [10b,10d,29,31]. In these prominent reports, starting from primary amines to higher-order amines such as secondary and tertiary amines, cyclic tertiary amines by means of diols, and *N*-heterocyclic compounds by employing functionalized amine substrates were obtained by transition-metal catalysis. In a similar manner, secondary amines and ammonia were applied for the same purpose. However, there are still very few reports in the literature on the ruthenium-carbene catalyzed *N*-alkylation of cyclic secondary amines based on hydrogen-borrowing protocols [10b,13c,32]. Therefore, the synthesis of five new half sandwich ruthenium-carbene complexes of the general formula [$RuCl_2(\eta^6$-*p*-cymene)(NHC)] (NHC = 1,3-dialkylbenzimidazol-2-ylidene), **2a-2e** were performed in this study. All ruthenium complexes were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy and elemental analysis techniques. The ruthenium complexes were tested as catalysts in the *N*-alkylation of cyclic secondary amines such as pyrrolidine and piperidine, and 4-methylaniline which was a primary aromatic amine with aliphatic and benzylic alcohols by hydrogen-borrowing process (Fig. 2).

2. Results and discussion

2.1. Preparation of benzimidazolium salts

The new **1b** and **1e** benzimidazolium salts as NHC ligand precursors were synthesized by the reaction of *N*-(alkyl)benzimidazole with different benzyl halides in chloroform at 60 °C for 24 h. **1a** [33], **1c** [25a] and **1d** [25b] NHC ligand precursors have been prepared according to the literature. The new **1b** and **1e** ligand precursors were confirmed by ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopies and elemental analysis techniques. As shown in Table 1, the FT-IR data clearly indicated that the new **1b** and **1e** benzimidazolium salts exhibit a characteristic $\nu_{(CN)}$ band typically at 1561 and 1557 cm^{-1}, respectively. In the ^{1}H NMR spectra, C(2)-*H* proton down-field resonance of **1b** and **1e** were observed as sharp singlets at δ = 11.72 and 11.18 ppm, respectively. In the ^{13}C NMR spectra, *C*(2)-carbon resonance of **1b** and **1e** salts were appeared at δ = 143.9 and 143.2 ppm, respectively as single signals. These spectroscopic values are in line with those found for other benzimidazolium salts of the literature [24c,25c,33].

2.2. Preparation of ruthenium-carbene complexes

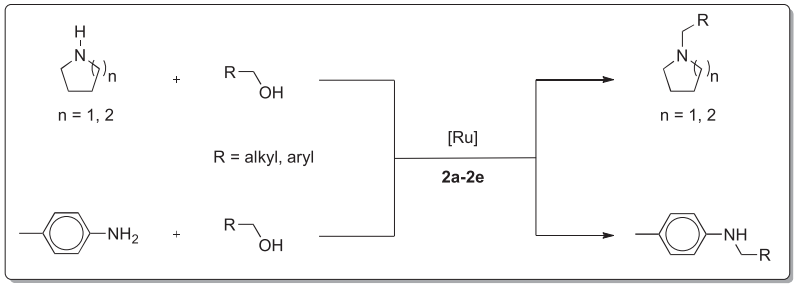
The new **2a-2e** ruthenium-NHC complexes were prepared by transmetallation of the corresponding silver-carbene adducts and [$RuCl_2$(*p*-cymene)]$_2$ dimer. The silver-carbene complexes, which should subsequently serve as a carbene-transfer agent, were synthesized by the reaction of Ag_2O with benzimidazolium salts (**1a-1e**) under exclusion of light. The non-isolated silver-carbene complexes were converted into the half-sandwich ruthenium-carbene complexes (**2a-2e**) in moderate to good yields after purification. Ruthenium-carbene complexes are very stable against air and moisture in the solid state. They are soluble in most organic solvents, such as dichloromethane, chloroform, methanol and acetonitrile, with the exception of non-polar ones, such as pentane, hexane and diethyl ether. Formation of half-sandwich ruthenium-carbene complexes is supported by NMR, FT-IR spectroscopies and microanalysis techniques. In the ^{1}H NMR spectra, the absence of C(2)-*H* down-field signals at δ = 10–12 ppm characteristic for the benzimidazolium salts indicates the formation of the expected ruthenium-carbene complexes. Also, there are two characteristic AB doublet signals at range of δ = 5–6 ppm corresponding to the methylene bridge protons of benzyl substituent, which become diastereotopic after coordination of the NHC ligands to the Ru atom. ^{13}C NMR chemical shifts provide a useful diagnostic tool for this type of metal-carbene complex. In the ^{13}C NMR spectra, the carbene signals of the ruthenium-carbene complexes were observed at δ = 190.1, 190.0, 191.6, 191.8 and 187.9 ppm, respectively. The FT-IR data clearly indicated that, ruthenium-carbene complexes exhibit a characteristic $\nu_{(CN)}$ stretching frequency peaks typically between 1454 and 1483 cm^{-1}. Due to the flow of electrons from the NHC ligand to the ruthenium, the C—N bond is weakened, and as a result, a decreasing in the $\nu_{(CN)}$ stretching frequency is expected. Also, the microanalysis datas of the ruthenium complexes agrees closely with the theoretical requirements of their structures. Half-sandwich ruthenium complexes (**2a-2e**) show typical spectroscopic signatures, which are in line with those recently reported for other similar type ruthenium-carbene complexes [24g,30,34].

All compounds were prepared according to general reaction pathway depicted in Scheme 1. The some physical and spectroscopic datas of all new compounds were summarized in the Table 1.

2.3. Determination of the optimum conditions for the N-alkylation of amines

In order to determine the optimum conditions in the reaction, alkylation of pyrrolidine with benzyl alcohol was investigated as a model reaction (Table 2). It is known in the literature that a stoichiometric amount of base is needed for *N*-alkylation of primary aromatic amines [31l,34]. But, due to the high basicity (pKa ~ 11) and high nucleophilic properties of secondary aliphatic amines compared to primary aromatic amines, the *N*-alkylation of such amines does not require the use of a stoichiometric amount of base [35].

Initially, after a series of trials to determine the most active catalyst



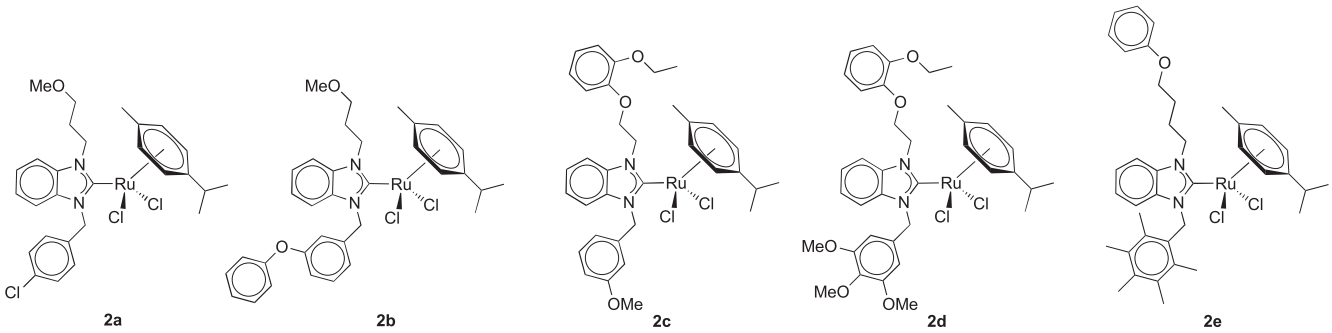


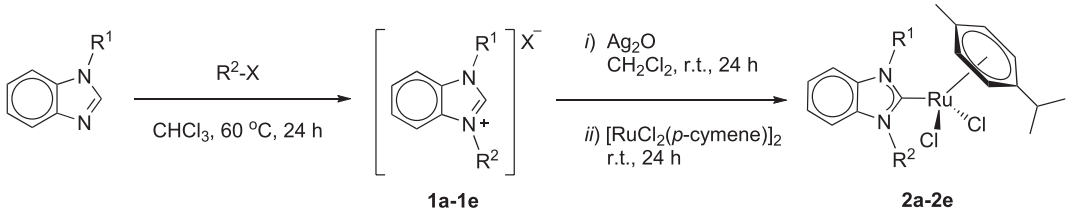
Fig. 2. *N*-Alkylation of primary and secondary amines with alcohols catalyzed by half-sandwich ruthenium complexes.

Table 1
Physical and spectroscopic properties of all new compounds.

Compound	Formula	Isolated yield[%]	M.p. [°C]	FT-IR $\nu_{(CN)}$[cm^{-1}]	C(2)-*H* ^{1}H NMR[ppm]	*C*(2) ^{13}C NMR[ppm]
1b	$C_{24}H_{25}ClN_2O_2$	75	121–122	1561	11.72	143.9
1e	$C_{29}H_{34}ClN_2O$	80	213–214	1557	11.18	143.2
2a	$C_{28}H_{33}Cl_3N_2ORu$	79	156–157	1471	–	190.1
2b	$C_{34}H_{38}Cl_2N_2O_2Ru$	54	127–128	1483	–	190.0
2c	$C_{35}H_{40}Cl_2N_2O_3Ru$	74	138–139	1468	–	191.6
2d	$C_{37}H_{44}Cl_2N_2O_5Ru$	66	124–125	1454	–	191.8
2e	$C_{39}H_{48}Cl_2N_2ORu$	82	190–191	1465	–	187.9

among the **2a-2e** catalysts (Table 2, entries 1–5), it was determined that the most active catalyst was the **2d** catalyst. Therefore, all other entries were performed in the presence of the **2d** catalyst. Later, lower reaction times were tested to investigate the effect of reaction time on conversion. When the reaction was carried out at 16 h, 94% conversion was observed (Table 2, entry 6), but when the reaction time was reduced to 8 h, the conversion was significantly reduced (Table 2, entry 7). No significant difference was observed on the conversion between the 24 h or the 16 h. Therefore, it was decided to carry out the reaction at 16 h as the optimum time. When the reaction was carried out in presence of 1 mol% catalyst loading under solvent-free conditions at 16 h (Table 2, entry 8), similar results were obtained with the reaction using toluene as the solvent. Therefore, the further reactions were carried out under solvent-free conditions. When the catalyst loading was reduced from 1 mol% to 0.5 mol%, the conversion dropped to 36%, but no noticeable effect on the selectivity of **3a**/**3′a** was observed (Table 2, entry 9).

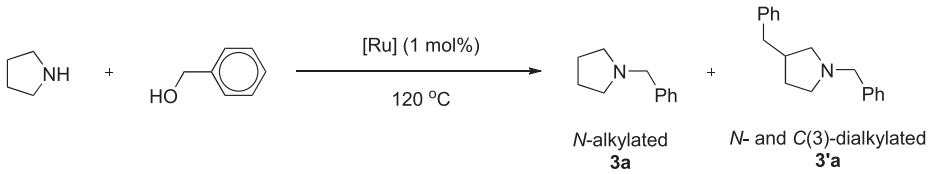
In the reaction of pyrrolidine with benzyl alcohol, *N*- and *C*(3)-dibenzylated pyrrolidine (**3′a**) can be observed as a side-product. In 2010, Bruneau and co-workers obtained the *N*- and *C*(3)-dibenzylated products as the main product using D-(+)-camphorsulfonic acid (CSA) as an additive [36]. In this context, CSA was also used as an additive to determine the effect on *N*- and *C*(3)-dibenzylated product formation.



	R^1	R^2	X
a,	$CH_2CH_2CH_2OMe$	$CH_2Ph(Cl)$-4	Cl
b,	$CH_2CH_2CH_2OMe$	$CH_2Ph(OPh)$-3	Cl
c,	$CH_2CH_2OPh(OEt)$-2	$CH_2Ph(OMe)$-3	Cl
d,	$CH_2CH_2OPh(OEt)$-2	$CH_2Ph(OMe)_3$-3,4,5	Br
e,	$CH_2CH_2CH_2CH_2OPh$	$CH_2Ph(Me)_5$-2,3,4,5,6	Cl

Scheme 1. Synthesis of NHC ligand precursors (**1a-1e**) and their half-sandwich ruthenium-carbene complexes (**2a-2e**).

Table 2
Influence of the reaction conditions for ruthenium-carbene catalyzed alkylation of pyrrolidine.[a]



Entry	[Ru]	Additive [mol-%]	Solvent	Time [h]	Conversion[b] [%]	Ratio of **3a/3'a**[c]
1	**2a**	None	Toluene	24	83	88/12
2	**2b**	None	Toluene	24	78	90/10
3	**2c**	None	Toluene	24	90	86/14
4	**2d**	None	Toluene	24	98	100/0
5	**2e**	None	Toluene	24	87	90/10
6	**2d**	None	Toluene	16	94	100/0
7	**2d**	None	Toluene	8	53	100/0
8	**2d**	**none**	**Solvent-free**	**16**	**94**	**100/0**
9[d]	**2d**	None	Solvent-free	16	36	100/0
10	**2d**	CSA (20)	Solvent-free	16	88	68/32
11	**2d**	CSA (40)	Solvent-free	16	90	54/46
12	**2d**	CSA (80)	Solvent-free	16	55	66/34

[a] Reaction conditions: [Ru] (0.01 mmol, 1 mol%), pyrrolidine (1.0 mmol), alcohol (1.5 mmol), no base, 120 °C.
[b] Conversions (%) were calculated according to pyrrolidine by GC analysis using dodecane as an internal standard.
[c] Ratio of *N*-alkylated and *N,C*(3)-dialkylated products were calculated by GC analysis.
[d] 0.005 mmol, (0.5 mol%) **2d** catalyst was used.

When 20 mol% CSA was used, 88% conversion was obtained in the reaction, and the *N*- and *C*(3)-dibenzylated product ratio increased to 32% (Table 2, entry 10). When the amount of CSA was doubled under similar conditions, it was observed that the ratio of *N*- and *C*(3)-dibenzylated product increased to 46% (Table 2, entry 11). Interestingly, when the amount of CSA was increased to 80 mol%, both the conversion and the dibenzylated product ratio decreased (Table 2, entry 12). In contrast to Bruneau's study, the use of CSA in this study did not significantly increase the formation of *N*- and *C*(3)-dibenzylated products. After these preliminary trials, it was concluded that the best conditions for *N*-alkylation were achieved without the use of additives under solvent-free conditions at 120 °C, 16 h.

2.4. *N*-Alkylation of amines with alcohols

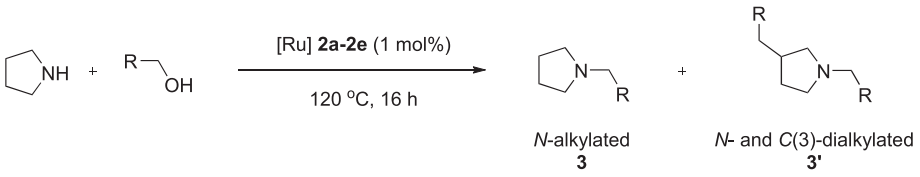
N-Alkylation of cyclic secondary amines such as pyrrolidine and piperidine, and primary aromatic amine such as 4-methylaniline with aliphatic and benzylic alcohols was evaluated using the determined optimum conditions (Table 3–5). In all cases, only *N*-monoalkylated amines were obtained as the main products. Since CSA was not used as an additive, *N*- and *C*(3)-dialkylated products were not observed in some cases. Conversions, selectivities and yields were determined by GC analysis. The main products of the reaction were purified by column chromatography, and they were characterized by NMR spectroscopy. Initially, the alkylation of pyrrolidine with aliphatic and benzylic alcohol derivatives was carried out in the presence of **2a-2e** catalysts under the determined optimum conditions (Table 3). In the studies conducted, it was observed that the reaction occurred with high conversion. In all cases, *N*-alkylated pyrrolidine derivatives as the main product were obtained with high yields. All the results of the alkylation of pyrrolidine are summarized in Table 3.

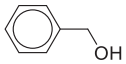
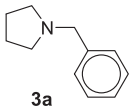
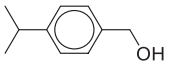
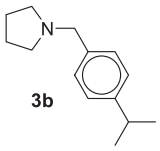
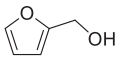
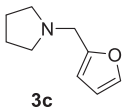
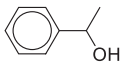
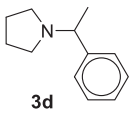
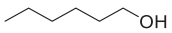
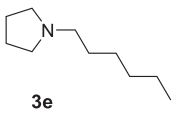
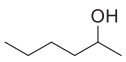
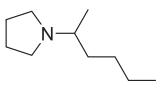
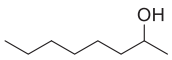
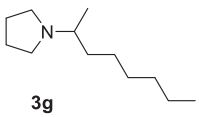
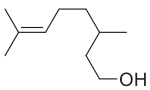
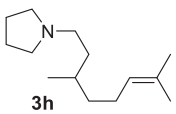
The reaction of pyrrolidine with benzyl alcohol was carried out in 71–94% conversions (Table 3, entries 1–5). Only *N*-benzyl pyrrolidine (**3a**) was obtained as product in the presence of **2d** catalyst in 85% GC yield (Table 3, entry 4). Similar results were obtained when 4-isopropylbenzyl alcohol was used (Table 3, entries 6–10). *N*-(4-isopropylbenzyl) pyrrolidine (**3b**) was obtained in 75% yield in the presence of **2d** catalyst. When heteroaromatic 2-furfuryl alcohol was used, only *N*-(furan-2-ylmethyl) pyrrolidine (**3c**) was obtained as product with **2b** and **2e** catalysts (Table 3, entries 12,15), while *N*- and *C*(3)-dialkylated product was observed with 22% selectivity in the presence of **2d** catalyst (Table 3, entry 14). Then the effect of aliphatic primary and secondary alcohols was examined. In general, the reaction was carried out at higher conversions with primary alcohols, while slightly lower conversions were obtained with secondary alcohols. For example, it is interesting to note that the less reactive secondary alcohol 1-phenylethanol reacted smoothly to give the *N*-(1-phenylethyl) pyrrolidine in 46–74% yield (Table 3, entries 16–20). The primary and secondary aliphatic alcohols proved to be less reactive but the condensation was also selective leading to the *N*-alkylated products. When 1-hexyl alcohol was used, *N*-(1-hexyl) pyrrolidine (**3e**) was obtained in 51–74% yields (Table 3, entries 21–25), while 2-hexyl alcohol was used, *N*-(2-hexyl) pyrrolidine (**3f**) was obtained in 47–68% yields (Table 3, entries 26–30). Similar results were observed when 2-octyl alcohol was used and moderate to high yields were obtained (Table 3, entries 31–35). In all cases except entry 32, *N*-(2-octyl) pyrrolidine (**3g**) was obtained with full selectivity. When Citronellol, which a natural acyclic monoterpenoid compound, was used, high yields were observed in all cases (Table 3, entries 36–40). The product *N*-(3,7-dimethyloct-6-en-1-yl) pyrrolidine (**3h**) was obtained in the presence of **2d** catalyst in 74% isolated yield.

Next, the scope of the reaction was extended to the six-membered piperidine substrate. Piperidine was *N*-alkylated by the benzylic alcohols and aliphatic primary and secondary alcohols with high conversion in similar conditions (Table 4).

High conversions were obtained when the benzyl alcohol was used with piperidine under solvent-free conditions (Table 4, entries 1–5). *N*-benzyl piperidine (**4a**) was obtained with 80% isolated yield in the presence of **2d** catalyst. Surprisingly, the use of benzyl alcohol led to a small amount of *N*- and *C*(3)-dialkylated product (about 27% ratio) with piperidine in presence of **2d** catalyst (Table 4, entry 4). Similar results were obtained when 4-isopropylbenzyl alcohol was used. In this case *N*-(4-isopropylbenzyl) piperidine (**4b**) was obtained in 61–80% GC yield (Table 4, entries 6–10). The 2-octyl alcohol, which an aliphatic

Table 3
Ruthenium-carbene catalyzed alkylation of pyrrolidine with alcohols.[a]



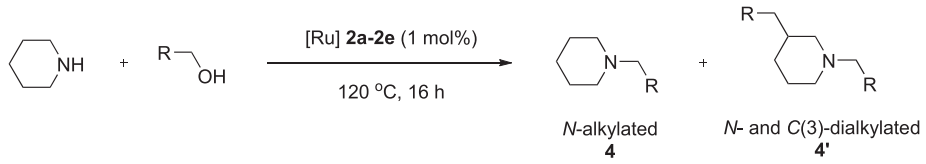
Entry	Alcohol	[Ru]	Main product	Conversion[b] [%]	Ratio of 3/3'[c]	Yield of 3[d] [%]
1		2a		78	90/10	60
2		2b		71	93/7	56
3		2c		85	89/11	72
4		2d		94	100/0	85 (80)
5		2e	3a	83	94/6	74
6		2a		69	98/2	55
7		2b		72	88/12	60
8		2c		81	100/0	73
9		2d		86	85/15	75 (70)
10		2e	3b	79	96/4	68
11		2a		81	95/5	70
12		2b		76	100/0	62
13		2c		86	95/5	73
14		2d		90	78/22	80
15		2e	3c	94	100/0	85 (72)
16		2a		62	90/10	46
17		2b		67	88/12	55
18		2c		80	94/6	68
19		2d		83	97/3	74 (70)
20		2e	3d	75	100/0	63
21		2a		66	97/3	51
22		2b		72	100/0	61
23		2c		88	89/11	74 (79)
24		2d		84	83/17	70
25		2e	3e	78	100/0	66
26		2a		58	95/5	47
27		2b		66	97/3	58
28		2c		72	100/0	60
29		2d		77	90/10	68 (65)
30		2e	3f	65	95/5	57
31		2a		60	100/0	52
32		2b		68	96/4	55
33		2c		70	100/0	55
34		2d		77	100/0	72 (65)
35		2e	3g	64	100/0	50
36		2a		66	98/2	58
37		2b		70	100/0	61
38		2c		81	100/0	69
39		2d		88	89/11	80 (74)
40		2e	3h	77	100/0	64

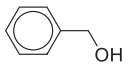
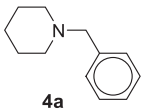
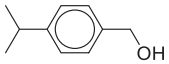
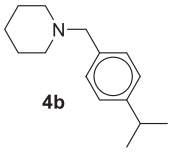
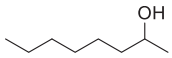
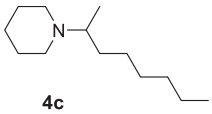
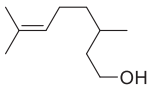
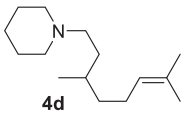
[a] Reaction conditions: [Ru] (**2a-2e**) (0.01 mmol, 1 mol%), pyrrolidine (1.0 mmol), alcohol (1.5 mmol), no base, no solvent, 120 °C, 16 h.
[b] Conversions (%) were calculated according to pyrrolidine by GC analysis using dodecane as an internal standard.
[c] Ratio of *N*-alkylated and *N,C*(3)-dialkylated products were calculated by GC analysis.
[d] Yields (%) were calculated by GC analysis and the number in parenthesis corresponds to the isolated yield after purification by column chromatography.

secondary alcohol, was also led to 59–92% conversion with perfect selectivity (Table 4, entries 11–15). *N*-(2-octyl) piperidine (**4c**) was abtained with 73% isolated yield in presence of **2e** catalyst (Table 4, entry 15). When Citronellol was used, high selectivity *N*-(3,7-dimethyloct-6-en-1-yl) piperidine (**4d**) was formed in the presence of **2b** and **2e** catalysts (Table 4, entries 17,20). This product was obtained in 80% isolated yield in the presence of **2d** catalyst (Table 4, entry 19). As previously observed with pyrrolidine, the primary and secondary aliphatic alcohols were less reactive and the corresponding tertiary amines were isolated in lower yields.

It must be noted that in the presence of a deprotonating reagent such as ^{t}BuOK or NaH in refluxing toluene, [RuX_2(arene)(NHC)] complexes have led to the selective formation of amides from primary and secondary amines [35]. But, the *N*-alkylation of primary and secondary amines was provided with 20 mol% of the weak base such as $NaHCO_3$ in presence of [$RuCl(PPh_3)$(*p*-cymene)(NHC)] complexes at 130 °C under solvent-free conditions [37]. In this catalytic system, the basic cyclic secondary amines might play the role of deprotonating reagent

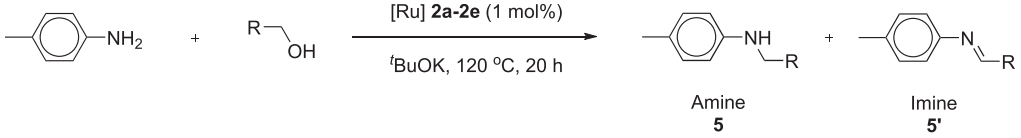
Table 4
Ruthenium-carbene catalyzed alkylation of piperidine with alcohols.[a]

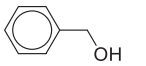
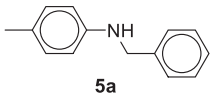
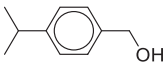
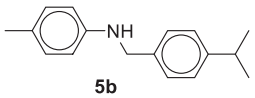
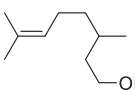
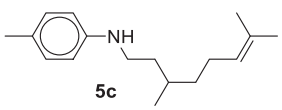


Entry	Alcohol	[Ru]	Main product	Conversion[b][%]	Ratio of 4/4'[c]	Yield of 4[d] [%]
1		2a		80	97/3	72
2		2b		76	95/5	56
3		2c		90	85/15	72
4		2d		97	83/27	85 (80)
5		2e	4a	91	95/5	83
6		2a		73	100/0	61
7		2b		79	95/5	67
8		2c		89	98/2	70
9		2d		93	85/15	80 (77)
10		2e	4b	80	96/4	71
11		2a		76	96/4	64
12		2b		59	96/4	45
13		2c		82	100/0	70
14		2d		92	88/12	78
15		2e	4c	90	100/0	80 (73)
16		2a		75	98/2	63
17		2b		70	100/0	59
18		2c		91	88/12	77
19		2d		98	94/6	86 (80)
20		2e	4d	90	100/0	79

[a] Reaction conditions: [Ru] (**2a-2e**) (0.01 mmol, 1 mol%), piperidine (1.0 mmol), alcohol (1.5 mmol), no base, no solvent, 120 °C, 16 h.
[b] Conversions (%) were calculated according to piperidine by GC analysis using dodecane as an internal standard.
[c] Ratio of *N*-alkylated and *N,C*(3)-dialkylated products were calculated by GC analysis.
[d] Yields (%) were calculated by GC analysis and the number in parenthesis corresponds to the isolated yield after purification by column chromatography.

Table 5
Ruthenium-carbene catalyzed mono-alkylation of 4-methyl aniline with alcohols.[a]



Entry	Alcohol	[Ru]	Main product	Conversion[b][%]	Ratio of 5/5'[c]	Yield of 5[d] [%]
1		2a		81	98/2	70
2		2b		86	100/0	73
3		2c		91	100/0	80
4		2d	5a	95	100/0	83 (79)
5		2e		87	100/0	73
6		2a		73	90/10	61
7		2b		59	78/22	47
8		2c		79	100/0	70
9		2d	5b	90	100/0	80 (75)
10		2e		86	98/2	75
11		2a		66	82/18	54
12		2b		75	96/4	61
13		2c		96	100/0	85 (81)
14		2d		92	100/0	80
15		2e	5c	87	100/0	75
	2a-2e					

[a] Reaction conditions: [Ru] (**2a-2e**) (0.01 mmol, 1 mol%), 4-methylaniline (1.0 mmol), alcohol (1.5 mmol), ^{t}BuOK (1.5 mmol), no solvent, 120 °C, 20 h.
[b] Conversions (%) were calculated according to 4-methylaniline by GC analysis using dodecane as an internal standard.
[c] Ratio of amine and imine were calculated by GC analysis.
[d] Yields (%) were calculated by GC analysis and the number in parenthesis corresponds to the isolated yield after purification by column chromatography.

which favours the formation of tertiary *N*-alkylated amines facilitated under solvent-free conditions. These results contrast with the *N*-alkylation of aromatic amines such as anilines by alcohols with similar catalytic systems based on [RuX_2(*p*-cymene)(NHC)] complexes, which required the use of a stoichiometric amounts of base. Due to the low basicity of primary aromatic amines such as 4-methylaniline, there is a need for the use of a stoichiometric amount of base for the *N*-alkylation of such amines [31l,34]. Therefore, the *N*-alkylation of 4-methylaniline was tested in presence of a stoichiometric amount of base under the determined optimum conditions. In these trials, ^{t}BuOK base, which is widely used in similar studies in the literature, was used [34a]. It is known in the literature that increasing the catalyst loading led to complete conversion but with more of the *N*,*N*-dialkylated product [32d]. It is clear that there is a correlation between the amines nucleophilicity and the overall reactivity. Electron-donating groups on the aniline make the aniline ring more reactive, while the electron-withdrawing groups reduce the reactivity of the aniline ring. In addition, the increased chain length and steric properties of the alcohol leads to the reaction advancing in favor of *N*-monoalkylated product formation [32d]. Therefore, *N*-monoalkylation of 4-methyl aniline occurred with high selectivity. (Table 5).

The reaction of 4-methyl aniline with benzyl alcohol gave the *N*-(benzyl)-4-methyl aniline (**5a**) with excellent selectivities in 81–95% conversions (Table 5, entries 1–5). This product was obtained with 79% isolated yield in the presence of **2d** catalyst (Table 5, entry 4). 4-Isoproylbenzyl alcohol afforded the corresponding *N*-monoalkylated product, *N*-(4-isopropylbenzyl)-4-methyl aniline (**5b**), for the all catalysts (Table 5, entries 6–10). When the reaction was carried out with Citronellol, the *N*-alkylamine product, *N*-(3,7-dimethyloct-6-en-1-yl)-4-methyl aniline (**5c**), gave in moderate to high GC yield (Table 5, entries 11–15). This product was obtained in 81% isolated yield in the presence of **2c** catalyst (Table 5, entry 13).

In the present work, the use of the oxygen functionalised *N*-aryl and *N*-alkyl benzimidazol-2-ylidene ligands was preferred. The chelating nature of these type ligands promotes production of highly stable ruthenium complexes. The hemilabile part of such ligands is capable of reversible dissociation to produce vacant coordination sites, allowing complexation of substrates during the catalytic cycle. At the same time the strong donor carbene moiety remains connected to the metal centre [28–30]. Using of the CSA was not have a significant effect on the formation of *N*- and *C*(3)-dialkylated products, contrary to similar studies in the literature [30a,31f,36]. Therefore, CSA was not used in catalytic studies and *N*-monoalkylated amine derivatives were obtained as the main product. Due to the high basicity of cyclic secondary amines, the use of a stoichiometric amount of base was not needed in all trials using these amines.

3. Conclusions

In summary, five new half-sandwich ruthenium-carbene complexes were synthesized, and they were characterized by various spectroscopic and analytical methods. The catalytic activities of the ruthenium-carbene complexes was tested for the *N*-alkylation of amines with alcohols by hydrogen-borrowing process. The catalytic studies carried out under solvent-free conditions were used various substrates such as aliphatic and benzylic alcohols. Thus, the *N*-alkylation of both the cyclic secondary amines and the primary aromatic amines was successfully carried out. The desired product was selectively obtained in moderate to high yields. By means of the present catalytic system, various higher-order cyclic and aromatic amines have been synthesized under mild and harmless conditions without producing wastes, and only water has released as by-product. Therefore, ruthenium-catalyzed *N*-alkylation of amines with alcohols through the borrowing hydrogen approach provides an economically and environmentally attractive procedure for the preparation of higher amines.

4. Experimental

4.1. General procedure for the preparation of NHC ligand precursors (*1a-1e*)

N-(Alkyl)-1*H*-benzimidazole derivative (5.0 mmol) was dissolved in degassed $CHCl_3$ (10 mL) and alkyl halide (5.0 mmol) was added under argon atmosphere. The reaction mixture was stirred at 60 °C for 24 h. Further, the volume of the reaction mixture was reduced up to 5 mL, and Et_2O (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid precipitate was washed with Et_2O (3 × 10 mL) and dried under vacuum. The crude product was recrystallized from EtOH/Et_2O mixture (1:4, *v/v*) and completely dried under vacuum. The new NHC ligand precursors **1b** and **1e** were isolated as air- and moisture-stable white solids with 75% and 80% yields, respectively. The **1a** [33], **1c** [25a] and **1d** [25b] NHC ligand precursors have already been reported in the literature. All the new NHC ligand precursors were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and elemental analysis techniques. For the ^{1}H NMR, ^{13}C NMR and FT-IR spectrums of the new **1b** and **1e** benzimidazolium salts see SI file, pages S1–S4.

4.1.1. 1-(3-Methoxypropyl)-3-(3-phenoxybenzyl)benzimidazolium chloride, (*1b*)

Yield: 1.533 g, 75% (white solid); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 2.31 (p, J = 5.6 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.22 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.44 (t, J = 5.3 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 4.71 (t, J = 6.7 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 5.89 (s, 2H, $NCH_2C_6H_4(OC_6H_5)$-3); 6.86–6.91 (m, 3H, arom C*H*s of NC_6H_4N); 6.99 (s, 1H, arom C*H* of NC_6H_4N); 7.07 (t, J = 7.4 Hz, 1H, arom C*H* of $NCH_2C_6H_4(OC_6H_5)$-3); 7.19–7.30 (m, 4H, arom C*H*s of $NCH_2C_6H_4(OC_6H_5)$-3); 7.52 (d, J = 8.0 Hz, 2H, arom C*H*s of $NCH_2C_6H_4(OC_6H_5)$-3); 7.56–7.61 (m, 1H, arom C*H* of $NCH_2C_6H_4(OC_6H_5)$-3); 7.75 (d, J = 8.1 Hz, 1H, arom C*H* of $NCH_2C_6H_4(OC_6H_5)$-3); 11.72 (s, 1H, NC*H*N). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ(ppm) = 29.6 ($NCH_2CH_2CH_2OCH_3$); 45.1 ($NCH_2CH_2CH_2OCH_3$); 51.0 ($NCH_2C_6H_4(OC_6H_5)$-3); 58.8 ($NCH_2CH_2CH_2OCH_3$); 68.9 ($NCH_2CH_2CH_2OCH_3$); 113.1, 113.7, 118.0, 118.8, 119.2, 122.7, 123.8, 127.1, 129.9, 130.8, 131.0, 131.8, 134.9, 156.4, 158.0 (arom. *C*s of NC_6H_4N and $NCH_2C_6H_4(OC_6H_5)$-3); 143.9 (NCHN). Elemental analysis calcd. (%) for $C_{24}H_{25}ClN_2O_2$ (M.w. = 408.93 g.mol^{-1}): C 70.49, H 6.16, N 6.85; found (%): C 70.66, H 6.28, N 6.99; (for the NMR and FT-IR spectrum of **1b** see SI file, pages S1–S2).

4.1.2. 1-(4-Phenoxybutyl)-3-(2,3,4,5,6-pentamethylbenzyl) benzimidazolium chloride, (*1e*)

Yield: 1.848 g, 80% (white solid); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.97 (p, J = 5.9 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 2.24, 2.28 and 2.30 (s, 15H, $NCH_2C_6(CH_3)_5$–2,3,4,5,6); 2.26 (p, J = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 4.04 (t, J = 5.8 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 4.85 (t, J = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 5.84 (s, 2H, $NCH_2C_6(CH_3)_5$–2,3,4,5,6); 6.82 (d, J = 8.0 Hz, 2H, arom. C*H*, $NCH_2CH_2CH_2CH_2OC_6H_4$); 6.93 (t, J = 7.3 Hz, 1H, arom. C*H*, $NCH_2CH_2CH_2CH_2OC_6H_4$); 7.25 (t, J = 7.9 Hz, 2H, arom. C*H*, $NCH_2CH_2CH_2CH_2OC_6H_4$); 7.30 (d, J = 8.5 Hz, 1H, arom. C*H*, NC_6H_4N); 7.50 (t, J = 7.8 Hz, 1H, arom. C*H*, NC_6H_4N); 7.60 (t, J = 7.8 Hz, 1H, arom. C*H*, NC_6H_4N); 7.74 (d, J = 8.3 Hz, 1H, arom. C*H*, NC_6H_4N); 11.18 (s, 1H, NC*H*N). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 17.0, 17.2 and 17.4 ($NCH_2C_6(CH_3)_5$–2,3,4,5,6); 26.1 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 26.5 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 47.4 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 48.2 ($NCH_2C_6(CH_3)_5$–2,3,4,5,6); 66.8 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 113.1, 113.8, 114.4, 120.9, 124.9 127.0, 127.1, 129.5, 131.5, 131.6, 133.5, 134.0, 137.3, 158.5 (arom. *C*s of NC_6H_4N, $NCH_2C_6(CH_3)_5$–2,3,4,5,6 and $NCH_2CH_2CH_2CH_2OC_6H_5$); 143.2 (NCHN). Elemental analysis calcd. (%) for $C_{29}H_{34}ClN_2O$ (M.w. = 462.05 g.mol^{-1}): C 75.38, H 7.42, N 6.06; found (%): C 75.53,

H 7.57, N 6.14; (for the NMR and FT-IR spectrum of **1e** see SI file, pages S3–S4).

4.2. General procedure for the preparation of the half-sandwich ruthenium-carbene complexes (**2a-2e**)

For the preparation of the ruthenium-carbene complexes (**2a-2e**), a solution of NHC ligand precursor (0.5 mmol), Ag_2O (0.25 mmol), activated 4 Å molecular sieves and anhydrous dichloromethane (10 mL) were added to a Schlenk tube under argon atmosphere. This solution was stirred at room temperature for 24 h in the dark conditions, and filtered through a Celite. After that, $[RuCl_2(p\text{-cymene})]_2$ dimer (0.25 mmol) was added to this solution under argon atmosphere, and this solution was stirred for 24 h at room temperature. End of the reaction, the solution was filtered through Celite and the all solvent was removed under reduced vacuum to afford the product as brown powder. The crude product was recrystallized from dichloromethane/*n*-pentane mixture (1:5, *v/v*). All new ruthenium-carbene complexes were isolated as air-stable and red-brown solids with 54–82% yields. For the ^{1}H NMR, ^{13}C NMR and FT-IR spectrums of the new **2a-2e** ruthenium-carbene complexes see SI file, pages S5–S14.

4.2.1. Dichloro-[1-(3-methoxypropyl)-3-(4-chlorobenzyl)benzimidazole-2-ylidene](p-cymene)ruthenium(II), (**2a**)

Yield: 0.245 g, 79% (red-brown solid); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.18 (d, J = 6.9 Hz, 6H, $CH(CH_3)_2$ of *p*-cymene); 1.93 (s, 3H, CH_3 of *p*-cymene); 2.09 (p, J = 5.3 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 2.87 (hept, J = 6.7 Hz, 1H, $CH(CH_3)_2$ of *p*-cymene); 3.37 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.53 (t, J = 5.3 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 4.94 (t, J = 6.6 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 5.31 (s, 2H, $NCH_2C_6H_4(Cl)$-4); 5.40–6.13 (m, 4H, arom. C*H*s of *p*-cymene); 6.89 and 7.50 (d, J = 8.0 Hz, 2H, arom. C*H*s of $NCH_2C_6H_2(Cl)$-4); 6.99–7.08 and 7.15–7.26 (m, 6H, arom. C*H*s of NC_6H_4N and $NCH_2C_6H_2(Cl)$-4). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 18.7 (CH_3 of *p*-cymene); 22.3 and 23.2 ($CH(CH_3)_2$ of *p*-cymene); 30.7 ($NCH_2CH_2CH_2OCH_3$); 30,9 ($CH(CH_3)_2$ of *p*-cymene); 48.0 ($NCH_2CH_2CH_2OCH_3$); 52.5 ($NCH_2C_6H_4(Cl)$-4); 58.9 ($NCH_2CH_2CH_2OCH_3$); 70.5 ($NCH_2CH_2CH_2OCH_3$); 83.0, 83.7, 86.0, 86.2 (arom. *C*s of *p*-cymene); 99.4, 109.2, 111.2, 111.5, 123.1, 123.2, 127.9, 128.9, 133.3, 135.2, 135.4, 135.9 (arom. *C*s of NC_6H_4N and $NCH_2C_6H_4(Cl)$-4); 190.1 (Ru-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{28}H_{33}Cl_3N_2ORu$ (M.w. = 621.01 g.mol^{-1}): C 54.16, H 5.36, N 4.51; found (%): C 54.35, H 5.25, N 4.40; (for the NMR and FT-IR spectrum of **2a** see SI file, pages S5–S6).

4.2.2. Dichloro-[1-(3-methoxypropyl)-3-(3-phenoxybenzyl)benzimidazole-2-ylidene](p-cymene)ruthenium(II), (**2b**)

Yield: 0.188 g, 54% (red-brown solid); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.24 (d, J = 6.9 Hz, 6H, $CH(CH_3)_2$ of *p*-cymene); 1.94 (s, 3H, CH_3 of *p*-cymene); 2.25–2.43 (m, 2H, $NCH_2CH_2CH_2OCH_3$); 2.91 (hept, J = 6.9 Hz, 1H, $CH(CH_3)_2$ of *p*-cymene); 3.43 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.58 (t, J = 5.0 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 4.96 (t, J = 6.9 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 4.54–4.56, 5.06–5.08, 5.31–5.33 and 5.44–5.46 (m, 4H, arom. C*H*s of *p*-cymene); 5.62–5.67 and 6.52–6.57 (m, 2H, $NCH_2C_6H_4(OC_6H_5)$-3); 6.59 (s, 1H, arom. C*H* of $NCH_2C_6H_4(OC_6H_5)$-3); 6.84–6.93 (m, 4H, arom. C*H*s of NC_6H_4N and $NCH_2C_6H_4(OC_6H_5)$-3); 7.02 (d, J = 8.1 Hz, 1H, arom. C*H*s of NC_6H_4N and $NCH_2C_6H_4(OC_6H_5)$-3); 7.09 (t, J = 7.4 Hz, 1H, arom. C*H* of $NCH_2C_6H_4(OC_6H_5)$-3); 7.16 (t, J = 7.6 Hz, 1H, arom. C*H* of $NCH_2C_6H_4(OC_6H_5)$-3); 7.24–7.30 (m, 4H, arom. C*H*s of NC_6H_4N and $NCH_2C_6H_4(OC_6H_5)$-3); 7.55 (d, J = 8.1 Hz, 1H, arom. C*H* of NC_6H_4N). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 18.5 (CH_3 of *p*-cymene); 21.6 and 23.5 ($CH(CH_3)_2$ of *p*-cymene); 30.7 ($NCH_2CH_2CH_2OCH_3$); 30,8 ($CH(CH_3)_2$ of *p*-cymene); 47.9 ($NCH_2CH_2CH_2OCH_3$); 52.4 ($NCH_2C_6H(CH_3)_4$–2,3,5,6); 58.9 ($NCH_2CH_2CH_2OCH_3$); 70.6 ($NCH_2CH_2CH_2OCH_3$); 82.3, 83.6, 85.7, 87.3 (arom. *C*s of *p*-cymene); 99.2, 108.8, 111.1, 111.5, 115.6, 117.5, 119.2, 120.7, 123.0, 123.1, 123.7, 129.8, 130.4, 135.0, 135.5, 139.7, 156.4, 158.0 (arom. *C*s of NC_6H_4N and $NCH_2C_6H_4(OC_6H_5)$-3); 190.0 (Ru-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{34}H_{38}Cl_2N_2O_2Ru$ (M.w. = 678.66 g.mol^{-1}): C 60.17, H 5.64, N 4.13; found (%): C 60.45, H 5.78, N 4.19; (for the NMR and FT-IR spectrum of **2b** see SI file, pages S7–S8).

4.2.3. Dichloro-[1-(2-(2-ethoxyphenoxy)ethyl)-3-(3-methoxylbenzyl) benz-imidazol-2-ylidene](p-cymene)ruthenium (II), (**2c**)

Yield: 0.262 g, 74% (red-brown solid); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.25 (d, J = 6.9 Hz, 6H, $CH(CH_3)_2$ of *p*-cymene); 1.45 (t, J = 7.0 Hz, 3H, $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 2.04 (s, 3H, CH_3 of *p*-cymene); 2.93 (hept, J = 6.7 Hz, 1H, $CH(CH_3)_2$ of *p*-cymene); 3.72 (s, 3H, $NCH_2C_6H_4(OCH_3)$-3); 4.09 (q, J = 7.0 Hz, 2H, $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 4.55 (t, J = 7.0 Hz, 2H, $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 5.07 (m, 1H, $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 5.21 (s, 2H, $NCH_2C_6H_4(OCH_3)$-3); 5.36–5.40 (m, 2H, $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2 and arom. C*H*s of *p*-cymene); 5.60–5.62 (m, 3H, arom. C*H*s of *p*-cymene); 6.58 (d, J = 8.2 Hz, 1H, arom. C*H*s of $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 6.68 (s, 1H, arom. C*H* of $NCH_2C_6H_4(OCH_3)$-3); 6.78–6.90 (m, 5H, arom. C*H*s of $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2 and $NCH_2C_6H_4(OCH_3)$-3); 7.02–7.26 (m, 4H, arom. C*H*s, NC_6H_4N); 8.05 (d, J = 8.2 Hz, 1H, arom. C*H*s of $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 15.1 ($NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 18.4 ($CH_3$ of *p*-cymene); 21.7 and 23.4 ($CH(CH_3)_2$ of *p*-cymene); 30,7 ($CH(CH_3)_2$ of *p*-cymene); 50.4 ($NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 52.6 ($NCH_2C_6H_4(OCH_3)$-3); 55.2 ($NCH_2C_6H_4(OCH_3)$-3); 63.9 ($NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 69.3 ($NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 83.5, 85.1, 85.2, 86.5 (arom. *C*s of *p*-cymene); 98.2, 108.5, 111.2, 111.9, 112.5, 114.1, 118.0, 120.9, 121.6, 123.2, 130.0, 135.3, 135.6, 139.3, 147.8, 148.7, 160.1 (arom. *C*s of NC_6H_4N, $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2 and $NCH_2C_6H_4(OCH_3)$-3); 191.6 (Ru-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{35}H_{40}Cl_2N_2O_3Ru$ (M.w. = 708.69 g.mol^{-1}): C 59.32, H 5.69, N 3.95; found (%): C 59.75, H 5.87, N 3.80; (for the NMR and FT-IR spectrum of **2c** see SI file, pages S9–S10).

4.2.4. Dichloro-[1-(2-(2-ethoxyphenoxy)ethyl)-3-(3,4,5-trimethoxylbenzyl)- benzimidazol-2-ylidene](p-cymene) ruthenium(II), (**2d**)

Yield: 0.254 g, 66% (red-brown solid); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.18 (d, J = 7.0 Hz, 6H, $CH(CH_3)_2$ of *p*-cymene); 1.35 (t, J = 7.0 Hz, 3H, $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 1.98 (s, 3H, CH_3 of *p*-cymene); 2.88 (hept, J = 6.9 Hz, 1H, $CH(CH_3)_2$ of *p*-cymene); 3.57 (s, 6H, $NCH_2C_6H_2(OCH_3)_3$–3,4,5); 3.74 (s, 3H, $NCH_2C_6H_2(OCH_3)_3$–3,4,5); 3.99 (q, J = 7.0 Hz, 2H, $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 4.45–4.51 (m, 2H, $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 4.98 (m, 1H, $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 5.19 (d, J = 5.9 Hz, 2H, $NCH_2C_6H_2(OCH_3)_3$–3,4,5); 5.31–5.36 (m, 2H, $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2 and arom. C*H*s of *p*-cymene); 5.56–5.71 (m, 2H, arom. C*H*s of *p*-cymene); 6.22 (s, 1H, arom. C*H* of *p*-cymene); 6.28 (s, 2H, arom. C*H*s of $NCH_2C_6H_2(OCH_3)_3$–3,4,5); 6.73–6.84 (m, 4H, arom. C*H*s, NC_6H_4N and $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 6.99 (d, J = 8.1 Hz, 1H, arom. C*H* of NC_6H_4N); 7.07 (t, J = 7.6 Hz, 1H, arom. C*H* of NC_6H_4N); 7.18 (t, J = 7.7 Hz, 1H, arom. C*H* of NC_6H_4N); 7.94 (d, J = 8.2 Hz, 1H, arom. C*H* of $NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 15.1 ($NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 18.4 ($CH_3$ of *p*-cymene); 21.8 and 23.4 ($CH(CH_3)_2$ of *p*-cymene); 30,7 ($CH(CH_3)_2$ of *p*-cymene); 50.4 ($NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 53.1 ($NCH_2C_6H_2(OCH_3)_3$–3,4,5); 56.2 and 60.9 ($NCH_2C_6H_2(OCH_3)_3$–3,4,5); 63.8 ($NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 69.1 ($NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2); 83.9, 84.7, 85.2, 86.9 (arom. *C*s of *p*-cymene); 98.1, 103.4, 108.8, 111.4, 112.5, 114.1, 120.9, 121.7, 123.1, 133.0, 135.2, 135.6, 137.2, 147.7, 148.7, 153.6 (arom. *C*s of NC_6H_4N,

$NCH_2CH_2OC_6H_4(OCH_2CH_3)$-2 and $NCH_2C_6H_2(OCH_3)_3$–3,4,5); 191.8 (Ru-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{37}H_{44}Cl_2N_2O_5Ru$ (M.w. = 768.74 g.mol^{-1}): C 57.81, H 5.77, N 3.64; found (%): C 58.05, H 5.93, N 3.56; (for the NMR and FT-IR spectrum of **2d** see SI file, pages S11–S12).

4.2.5. Dichloro-[1-(4-phenoxybutyl)-3-(2,3,4,5,6-pentamethylbenzyl) benz-imidazole-2-ylidene](p-cymene)ruthenium (II), (2e)

Yield: 0.300 g, 82% (red-brown solid); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.22 (d, J = 5.8 Hz, 6H, $CH(CH_3)_2$ of *p*-cymene); 2.03–2.12 (m, 22H, $NCH_2CH_2CH_2CH_2OC_6H_5$, $NCH_2CH_2CH_2CH_2OC_6H_5$, $NCH_2C_6(CH_3)_5$–2,3,4,5,6 and CH_3 of *p*-cymene); 2.93 (hept, J = 6.8 Hz, 1H, $CH(CH_3)_2$ of *p*-cymene); 3.97–4.08 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 5.19 (t, J = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 5.46 (s, 2H, $NCH_2C_6(CH_3)_5$–2,3,4,5,6); 4.94–6.06 (m, 4H, arom. C*H*s of *p*-cymene); 6.86 and 7.32 (d, J = 8.0 Hz, 4H, arom. C*H*s of $NCH_2CH_2CH_2CH_2OC_6H_4$); 7.02 (t, J = 7.7 Hz, 1H, arom. C*H* of $NCH_2CH_2CH_2CH_2OC_6H$); 6.72 and 7.21 (t, J = 7.8 Hz, 4H, arom. C*H*s of NC_6H_4N). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 16.9, 17.2 and 17.3 ($NCH_2C_6(CH_3)_5$–2,3,4,5,6); 18.8 (CH_3 of *p*-cymene); 21.9 and 23.4 ($CH(CH_3)_2$ of *p*-cymene); 26.6 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 27.5 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 30.9 ($CH(CH_3)_2$ of *p*-cymene); 49.9 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 52.2 ($NCH_2C_6(CH_3)_5$–2,3,4,5,6); 67.3 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 83.4, 84.3, 85.9, 86.5 (arom. *C*s of *p*-cymene); 99.0, 108.5, 110.3, 111.9, 114.6, 120.7, 122.1, 122.6, 129.2, 129.5, 135.1, 135.5, 135.8, 158.9 (arom. *C*s of NC_6H_4N, $NCH_2C_6(CH_3)_5$–2,3,4,5,6 and $NCH_2CH_2CH_2CH_2OC_6H_5$); 187.9 (Ru-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{39}H_{48}Cl_2N_2ORu$ (M.w. = 732.80 g.mol^{-1}): C 63.92, H 6.60, N 3.82; found (%): C 64.13, H 6.77, N 3.88; (for the NMR and FT-IR spectrum of **2e** see SI file, pages S13–S14).

4.3. General procedure for the ruthenium-carbene catalyzed N-alkylation of amines

Amine (1.0 mmol) and alcohol (1.5 mmol), (and ^{t}BuOK (1.5 mmol) for 4-methylaniline), were added to a Schlenk tube under argon atmosphere. Subsequently, the ruthenium-carbene catalyst (**2a-2e**) (0.01 mmol, 1 mol%) was added to stirred solution in a Schlenk tube, and the closed Schlenk tube was stirred at 120 °C (oil bath temperature). End of the reaction, the solution was cooled to room temperature and dichloromethane (2 mL) was then added to the crude mixture. This solution was used for GC analysis and the resulting *N*-monoalkylated amines were purified and isolated by column chromatography (eluent: chloroform/MeOH). Yields (%) were calculated according to amines using dodecane as an internal standard. The **3a** [10b,29,31a], **3b** [31b], **3c** [10b,10d], **3d** [10d,29,31c], **3e** [29,31d], **3g** [31e], **3h** [31f], **4a** [29,31g,31h], **4b** [31i], **4c** [29], **4d** [31j,31k], **5a** [31l], **5b** [31l] and **5c** [31l] *N*-monoalkylated amines have already been reported in the literature. Only *N*-(2-hexyl) pyrrolidine (**3f**) is new. The chemical characterizations of the all the *N*-monoalkylated amines were made by NMR spectroscopy. NMR spectrums of the corresponding *N*-monoalkylated amines are available in the SI file, pages S15-S29.

4.3.1. N-(2-hexyl) pyrrolidine, (3f)

Yield: 0.116 g, 75%; (pale yellow oil); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 0.94 (t, J = 7.0 Hz, 3H); 1.26–1.41 (m, 4H); 1.44 (d, J = 6.5 Hz, 3H); 1.86–2.05 (m, 4H); 2.21–2.28 (m, 2H); 2.85 (p, J = 7.0 Hz, 2H); 3.10–3.16 (m, 1H); 3.73 (p, J = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 13.8, 15.4, 22.3, 23.8, 28.2, 31.8, 50.4, 50.7, 60.7; (for the NMR spectrum of **3f** see SI file, page S20).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2019.119163.

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