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Research paper

# Ru(II)-NHC catalysed *N*-Alkylation of amines with alcohols under solvent-free conditions

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ARTICLE INFO

Dedicated to Professor Maurizio Peruzzini on the occasion of his 65th birthday and contribution to the transition metal chemistry.

*Keywords:*
Amine
Hydrogen auto-transfer method
*N*-alkylation
Ru(II)-NHC

ABSTRACT

The reaction of $[RuCl_2(p\text{-cymene})]_2$ with *in situ* prepared Ag-*N*-heterocyclic carbene (NHC) complexes yields a series of $[RuCl_2(p\text{-cymene})(NHC)]$ complexes (**2**). All of the complexes have been characterised by elemental analysis, and $^1H$ NMR and $^{13}C$ NMR spectroscopies. These complexes have been tested for the *N*-alkylation of aromatic amines with arylmethyl alcohols under neat conditions in the presence of KO*t*Bu at 120 °C. Compounds (**2**) are stable and have high catalytic/selective activity for the *N*-alkylation reactions of primary amines to afford secondary amines.

## 1. Introduction

*N*-Heterocyclic carbenes have been used in recent years as an alternative to phosphine ligands in organometallic chemistry for homogeneous catalyst synthesis [1]. Unlike phosphine ligands, NHC ligands are more desirable because they have good σ-donor properties, low toxicity and can be more easily synthesised. The tunable character of NHCs allows easy control of the electronic and steric properties at the metal centre. As a result, NHC complexes have emerged as versatile tools in homogenous catalysis. *N*-Heterocyclic carbenes play a key role in the catalytic form of organic synthesis such as C—H activation, C—C, C—O, and C—N bond formation [2–6].

Amines are extensively used as pharmaceuticals and synthetic intermediates [7,8]. They can be synthesised by various stoichiometric and catalytic methods. The stoichiometric methods produce large amounts of waste. Furthermore, *N*-alkylation with alkyl halides and reactions containing strong reducing agents are particularly unfriendly to the environment, as these materials are highly toxic. Many of the reported methods (both catalytic and non-catalytic) have drawbacks with selectivity. The selectivity to the desired secondary amines is generally low in the *N*-alkylation with alkyl halides because the nucleophilicity of amines is increased by the *N*-alkylation, resulting in the formation of undesired tertiary amines and alkylammonium halides as byproducts [9–11].

More environmentally benign outcomes are obtained by metal-catalysed *N*-alkylation of primary amines with either alcohols or amines. These methods all have advantages and disadvantages, and there is still room for improvement [12]. The advantage of the procedure in comparison with the *N*-alkylation with alkyl halides is the high selectivity to the desired. However, these systems have disadvantages such as the recovery and reuse of expensive catalysts and/or the indispensable use of cocatalysts such as bases and stabilising ligands.

The borrowing hydrogen (BH) or the hydrogen auto-transfer method is a tandem process, where alcohols are dehydrogenated followed by base-mediated condensation of the resulting carbonyls with an amine nucleophile; subsequently the imine intermediate product is reduced. This procedure can be carried out under milder conditions at atmospheric pressures as it does not require additional hydrogen. It has many advantages over conventional methods when it comes to selectivity, cost, efficiency, and environmental considerations: only water emerges

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as a by-product [13]. All of these features make this method attractive for environmentally friendly and green chemistry. It is important from both industrial and academic points of view to improve selectivity and productivity by developing new and effective catalysts.

Grigg [14] and Watanabe [15] initially performed Ru-catalysed *N*-alkylation. More recently, better catalytic systems have been reported: these homogenous catalysts for alcohol amination are based on complexes of Ru, Ir, Fe, Co, Mn, Cu, Pd, Ni and Cr containing different ligands [16–29]. In the past several years, we have synthesised several NHC complexes bearing symmetrical or unsymmetrical benzyl groups with various alkyl substituents on the benzene ring. Their diverse structures could tune the properties of the corresponding complexes [30,31]. The incorporation of alkyl-substituents in the NHC ligand provides soluble catalyst complexes. Also, the electron-donating ability of the ligands greatly affects the redox potential of the transition metal complex and influences the reactivity of the metal centre. In this work, Ru(II) complexes **2** based on the imidazole/ benzimidazole skeleton was synthesised and the catalytic properties for BH were investigated.

## 2. Results and discussions

In this study, we used imidazolium and benzimidazolium salts (**1**) containing 4-(1-adamantylbenzyl substituent(s), which are readily synthesised precursors to these NHC ligands. The subsequent formation of Ag-NHC complexes has proved simple. The *in situ* reaction of the Ag-NHC complexes with $[RuCl_2(p\text{-cymene})]_2$ in dichloromethane afforded Ru-NHC complexes (**2a-2d**). The obtained Ru-NHC complexes were characterised by elemental analysis, $^1$H NMR and $^{13}$C NMR spectroscopies. These complexes are effective precatalysts for the alkylation of aromatic amines with different alcohols, in neat conditions.

### 2.1. Preparation of imidazolium salt, *1a*

The known compound 4-(1-adamantylbenzyl) bromide [32] was heated with 1-methylimidazole to obtain **1a**. 1-Methyl-3-(4-adamantylbenzyl)imidazolium bromide (**1a**) is air and moisture stable. **1a** is soluble in chlorinated solvents, alcohols, and water. The spectral properties of the imidazolium salt are similar to those of other reported imidazolium salts [33]. In the $^1$H NMR spectrum of **1a**, the NC*H*N proton appears as a singlet at 10.41. The signal of benzylic and aromatic hydrogens of adamantyl group appeared at 7.21–7.37 ppm. Protons of imidazole CH=CH appear as singlets at 5.45 and 5.47 ppm. The other signals of adamantyl group appear as singlet 1.74 and 2.02 ppm and quartet 1.66 ppm. The signal of methyl group as singlet 4.03 ppm.

### 2.2. Preparation of benzimidazolium salts

According to the literature [32,34], ligand precursors (**1b-1d**) were synthesised by quaternisation of 1-(4-adamantylbenzyl)-benzimidazole in DMF with corresponding benzyl bromides in a nearly quantitative yield, 88–90%. The salts are stable in solid-state. All salts are soluble in chlorinated solvents, alcohols, and water. The NC*H*N protons appear in the $^1$H NMR range of **1b-1d** at 11.40, 11.76 and 10.82 ppm, respectively, and these downfield signals confirm the formation of the benzimidazolium salts. The $^1$H NMR shifts of **1b-1d** are identical to those of other characterised benzimidazolium salts [35].

### 2.3. Preparation of ruthenium-carbene complexes *2a-2d*

NHC complexes are prepared using a variety of methods. One of the most useful approaches in this regard is transmetalation with Ag-NHC complexes. The use of silver-carbene complexes as a carbene transfer agent avoids complicated working difficulties. Transmetalation reactions can often be conducted under aerobic conditions; this method can be successfully extended to metals such as Cu, Au, Pd, Ni, Pt, Rh, Ru and Ir [36].

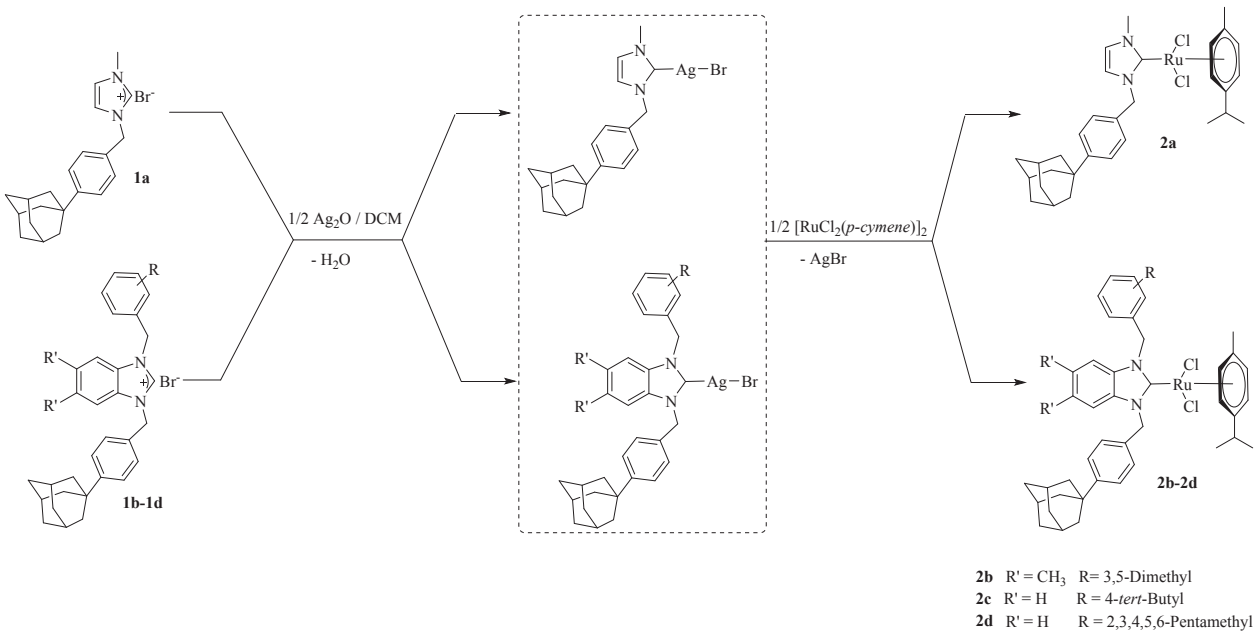
The new $[RuCl_2(p\text{-cymene})(NHC)]$ complexes (**2a-2d**) were prepared using a two-step process by transmetalling the respective silver-NHC derivatives (Scheme 1). Without isolation, the silver-NHC complexes were used *in situ*. Then, adding $[RuCl_2(p\text{-cymene})]_2$ to the mixture gave orange-brown complexes with good yields (70–78%). Ruthenium carbene complexes (**2a-2d**) are soluble in solvents such as chloroform, dichloromethane; and tetrahydrofuran, but not in nonpolar solvents. The structure of **2a-2d** complexes was confirmed by $^1$H and $^{13}$C NMR pectra. The characteristic downfield signals for the NC*H*N protons of the corresponding salts **1a-1d** disappeared in the $^1$H NMR spectra of complexes **2a-2d**. The aromatic protons of benzimidazole were seen as a multiplet at δ between 6.19 and 7.38 ppm in the $^1$H NMR spectrum. –CH- Protons of *p*-cymene group on all complexes (**2a-2d**) are seen as heptets in the range from 2.58 to 2.91 ppm. Methylic protons of *iso*butyl group on *p*-cymene resonated between 1.13, 1.14, 1.22 and 1.25 as doublets while methyl protons on *p*-cymene were detected as singlets at 2.06, 1.89 and 1.90 ppm. The proton signals of adamantyl groups were observed at 1.60–1.89 ppm. The complexes exhibit $^{13}$C chemical shifts of carbene carbon at 174.3, 189.0, 191.4 and 190.2 ppm, respectively. The data are close to those reported for other Ru-NHC complexes [31].

### 2.4. The N-alkylation of amines with alcohols

Secondary amines can be synthesised by many different methods. Reactions for their synthesis include the alkylation of amines with alkyl halides [37–39], the direct reductive amination of ketones and aldehydes [40] and the hydroamination of unsaturated hydrocarbons with amines [41,42]. These methods generally require environmentally harmful organic solvents, alkyl halides and/or stoichiometric quantities of reducing agents. In recent decades, much attention has focused on the use of inexpensive and low toxicity alcohols as the alkylation reagent [43]. The *N*-alkylation of amines with alcohols presents a green method for the synthesis of substituted amines that have substantial importance in synthetic applications. Ru- and Ir catalysed amine alkylation by alcohol has been previously reported by several groups [13].

Here, we used the optimised conditions for the catalytic reaction, which were determined in our previous works [30a,31]. In a standard experiment, KO*t*Bu (1 mmol), aromatic amine (1 mmol), alcohol derivative (1.5 mmol), and the Ru-NHC complex **2a-2d** (0.025 mmol) were added to the Schlenk tube under an inert atmosphere. The sealed Schlenk tube was stirred at 120 °C for 24 h. The reaction mixture was cooled to room temperature at the end of the reaction, before $CH_2Cl_2$ (2 mL) was added, and filtered through a short $SiO_2$ pad. The filtrate was analysed by GC. The yields were based on the corresponding aniline. The reactions were performed at a molar ratio of 1:0.025:1 aniline/precatalyst /base (S/C/base). It is worth noting that when the excess of benzyl alcohol (5 mmol) is used, only the secondary amine is formed in the catalytic reaction.

The *N*-alkylation of aniline, 2,4-dimethyl aniline, 4-(trifluoromethyl) aniline with the alcohols (benzyl alcohol, 4-methybenzyl alcohol, 4-methoxybenzyl alcohol, furfuryl alcohol, and 3,4-dimethoxybenzyl alcohol) was investigated using **2a-d** precatalysts to obtain the secondary amines under reaction conditions. Table 1 summarises the *N*-alkylation of arylamines with benzyl alcohols. When the reaction of aniline with benzyl alcohol was performed by the complex **2a-2d**, *N*-benzylaniline was obtained as a major product (Table 1, entry 1). For example, when complex **2a** was used as the precatalyst, 93% conversion with an amine/imine ratio of 98/2 was observed. Examination of the table shows that conversions are relatively low in the case of sterically hindered 2,4-dimethylaniline (Table 1, entries 6–10). We obtained the corresponding *N*-benzyl-2,4-dimethylaniline with 60–100% selectivity in 48–98% conversions (Table 1, entries 6–10). In this reaction when **2b** complex was used as the precatalyst, 96% conversion with an amine/imine ratio of 83/17 was observed (Table 1, entry 6). Alkylation reactions with arylmethyl alcohols, bearing electron-donating methyl and methoxy groups resulted in high conversion mainly amine was obtained




**Scheme 1.** Synthesis of [$RuCl_2$(*p*-cymene)(NHC)] complexes.

(Table 1, entries 2–4) and complex **2a** was the most efficient precatalyst. When 4-methylbenzyl alcohol is used as an alkylating agent, *N*-(4-methylbenzyl)aniline could be obtained in high conversion (Table 1, entry 2). When **2a** complex was used as the precatalyst, full conversion with mono-alkylated *N*-alkylaniline was formed selectively.

The amine with an electron-withdrawing group like -$CF_3$ has been almost converted to an *N*-alkylated product (up to 100%) with arylmethyl alcohols using **2a-2d** as a precatalyst (Table 1, entries 11–14). The electron-donating substituents like Me and OMe on both benzyl alcohol and aniline have significantly improved the selectivity of mono-alkylated amine products under the same conditions. All of the reactions using 3,4-dimethoxybenzyl alcohol resulted in the selective formation of mono-alkylated aniline in high conversions (Table 1, entry 4). When the reaction was carried out in the presence of **2a** as the precatalyst, full conversion was obtained with mono-alkylated *N*-alkylaniline formed selectively. The results are similar to those of other aniline derivatives. Similar trends for the other Ru(II) systems carrying NHC ligands have been reported [30a]. When the furfuryl alcohol was used as an alkylating agent, aniline and 2,4-dimethyl aniline gave corresponding mono-alkylated amine with 100% selectivity for all complexes **2a-d** (Table 1, entries 5, 10). In all of the reactions *N*-(2-furufurilmethyl)aniline was obtained as a major product, and very low imine formation ratio (selectivity of imine < 5%) was observed (Table 1, entries 15, 20).

The *N*-alkylation of 2-aminopyridine with the same alcohols (benzyl alcohol, 4-methybenzyl alcohol, 4-methoxybenzyl alcohol, furfuryl alcohol and 3,4-dimethoxybenzyl alcohol) was also investigated by using **2a-d** precatalysts to obtain *N*-alkylated amines under the same conditions. 2-(*N*-Alkylamino)pyridines were obtained in good to excellent selectivity in the presence of 2.5 mol% precatalysts. Also, under these catalytic conditions, the heteroaromatic moiety in 2-aminopyridine has also been well tolerated. 2-Aminopyridine was efficiently alkylated with 4-methybenzyl alcohol for all complexes **2a-d** with 100% selectivity (Table 1, entry 17). The reaction of 2-aminopyridine with benzyl alcohol, 4-methoxybenzyl alcohol, furfuryl alcohol and 3,4-dimethoxybenzyl alcohol also gave corresponding products in conversions from 95 to 100%.

## 3. Conclusion

A series of imidazolium/benzimidazolium salts, with the 1-adamantyl substituent at the C-4 positions of the benzyl rings, was synthesized. *N*-Heterocyclic carbene based ruthenium(*p*-cymene) complexes **2a-2d** were prepared *in situ* by reacting Ag(I)-NHC complexes with [$RuCl_2$(*p*-cymene)]$_2$ in dichloromethane at room temperature. The catalytic activity of the resulting Ru(II) complexes was evaluated in the alkylation of aniline derivatives via arylmethyl alcohols. We thought that Ru-NHC complexes would be the better catalyst due to the steric hindrance of the adamantyl group. But the catalytic results of *N*-alkylation reactions are not so different than others in our previous work. Substitution of the aromatic rings at the C-4 position of the NHC ligand did not reveal a notable enhancement of the catalytic reactions.

## 4. Experimental section

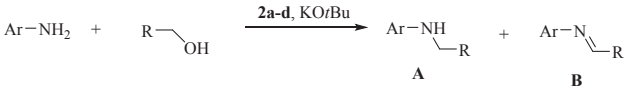
### 4.1. Materials

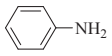
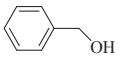
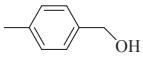
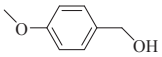
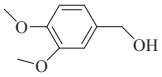
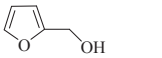
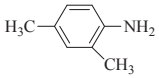
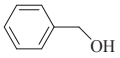
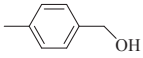
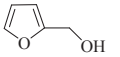
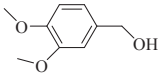
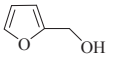
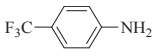
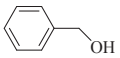
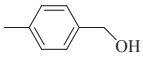
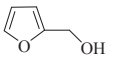
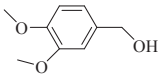
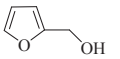
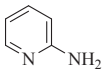
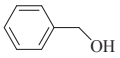
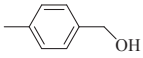
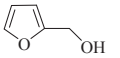
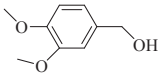
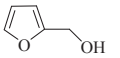
All reactions were performed using normal Schlenk techniques under argon in flame-dried glassware. Chemicals and solvents were purchased from Sigma–Aldrich, and Merck. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: $Et_2O$ (Na/K alloy), $CH_2Cl_2$ ($P_4O_{10}$), hexane, toluene (Na).

### 4.2. Apparatus and instruments

Schlenk line technique was used for performing all the synthesis and catalytic reactions. $^1$H NMR and $^{13}$C NMR spectra were recorded using a Bruker Avance AMX spectrometer operating at 400 MHz ($^1$H), 100 MHz ($^{13}$C) in $CDCl_3$ and DMSO-$d_6$ with tetramethylsilane as an internal reference. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ a downfield from tetramethylsilane ($\delta = 0.00$) as an internal standard. Coupling constants (J values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal. Elemental analyses were performed by LECO CHNS-932 elementary chemical analyzer. For the measurement of catalytic results (conversion and yield), Shimadzu GC 2025 with the specification of GC-FID sensor, column of RX-5 ms which have 30 m length, 0.25 mm diameter and 0.25 μM film thickness was used. Column chromatography was performed using silica gel 60 (70–230 mesh). Solvent ratios are given as v/v.

**Table 1**
*N*-alkylation of arylamine derivatives with different aryl methyl alcohols[a].




| Entry | Ar-$NH_2$ | Alcohol | [Ru] Conversion[b] (Yield A:B%) | | | |
|---|---|---|---|---|---|---|
| | | | 2a | 2b | 2c | 2d |
| 1 |  |  | 93 (98/2) | 99(81/19) | 96(89/7) | 98(71/29) |
| 2 | |  | 100(100/-)85[c] | 94(72/28) | 98(76/34) | 96(100/0) |
| 3 | |  | 98(90/10) | 99(65/35) | 89(100/-) | 86(91/9) |
| 4 | |  | 100(100/-) | 98(95/5) | 94(100/-) | 91(100/-) |
| 5 | |  | 100(100/-) | 100(100/-) | 97(100/-) | 89(100/-) |
| 6 |  |  | 94(60/40) | 96(83/17) | 96 (80/20) | 87(74/26) |
| 7 | |  | 91(77/22) | 96(89/11) | 78(95/5) | 92(86/14) |
| 8 | |  | 74(100/-) | 80(100/-) | 81(98/2) | 87(72/28) |
| 9 | |  | 90(90/10) | 98(96/4) | 88(91/9) | 91(92/8) |
| 10 | |  | 48(100/-) | 72(100/-) | 61(100/-) | 76(100/-) |
| 11 |  |  | 93(100/-) | 96(100/-) | 98 (80/20) | 87(100/-) |
| 12 | |  | 98(51/46) | 100(100/-) | 99(95/5) | 92(90/10) |
| 13 | |  | 94(98/2) | 96(80/20) | 89(77/33) | 97(92/8) |
| 14 | |  | 98(72/28) | 94(94/6) | 98(75/25) | 96(91/9) |
| 15 | |  | 88(97/3) | 88(99/1) | 79(100/-) | 92(100/-) |
| 16 |  |  | 98(100/-)80[c] | 99(93/7) | 100(100/-) | 98(100/-) |
| 17 | |  | 100(100/-) | 100(100/-) | 100(100/-) | 100(100/-) |
| 18 | |  | 100(100/-) | 100(100/-) | 99(98/2) | 99(98/2) |
| 19 | |  | 100(93/7) | 100(100/-) | 96(96/4) | 100(92/8) |
| 20 | |  | 95(96/4) | 99(100/-) | 96(100/0) | 97(100/-) |

[a]Reaction conditions: Complexes **2a-d (**0.025 mmol, 2.5 mol %), arylmethyl alcohol (1.5 mmol), aromatic amine (1 mmol), KO*t*Bu (1 mmol), 120 °C, 24 h. The conversions and the selectivities were determined by GC and dodecane were used as in internal standard. [b]Refers to arylamine's conversion to secondary amine and imine. [c]Isolated yield.

### 4.3. Synthesis

#### 4.3.1. Preparation of 4-benzyladamantyl bromide

4-(1-Adamantylbenzyl bromide was synthesized according to the literature [32].

#### 4.3.2. 1-Methyl-3-[4-(1-adamantyl]benzylimidazolium bromide, **1a**

Imidazolium salt **1a** was prepared accordingly known methods [33]. A solution of 1-methylimidazole (10 mmol) and 4-(1-adamantyl)benzyl bromide (10 mmol) in DMF (5 mL) was heated to 80 °C for 2 days. The solution was allowed to cool room temperature and the participants were treated with diethyl ether and washed with it. Solid was solved in DCM, and white solid crystals were obtained by addition of diethyl ether. Yield: 90%. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.66 [q, 6H, $J$ = 8 Hz, $H_{Ad}$], 1.74 [s, 6H, $H_{Ad}$], 2.02 [s, 3H, $H_{Ad}$], 4.03 [s, 3H, NC$H_3$], 5.45 [C$H_2$C$_6$H$_4$Ad], 7.21 and 7.29 [s, 2H, NC$H$CHN], 7.23–7.37 [m, 4H $CH_2C_6H_4$Ad], 10.41 [s, 1H, NC$H$N].$^{13}$C NMR (100 MHz, DMSO-$d_6$, 25 °C): $\delta$ = 29.9 [NC$H_3$], 30.7, 31.5, 33.7, 41.6, 42.9, 49.4 [$C_{Ad}$], 50.8 [$CH_2C_6H_4$Ad], 125.3 [s, 2H, NC$H$CHN], 128.8, 134.8 [$CH_2C_6H_4$Ad], 151.2 [NCHN]. Anal. Calc. for $C_{21}H_{27}N_2Br$: C, 65.11; H, 7.03; N, 4.46. Found: C, 65.28; H, 7.24; N, 4.30%.

The following salt precursors were synthesized according to the literature [32]:

1-[4-(1-Adamantyl)benzyl]-3-(3,5-dimethylbenzyl)-5,6-dimethylbenzimidazolium bromide, **1b**
1-[4-(1-Adamantyl)benzyl]-3-(4-*tert*-butylbenzyl)benzimidazolium bromide, **1c**
1-[4-(1-Adamantyl)benzyl]-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium bromide, **1d**

#### 4.3.3. Dichloro-[1-methyl-3-(4-adamantylbenzyl)imidazol-2-ylidene](p-cymene) ruthenium(II), **2a**

$Ag_2O$ (0.54 mmol) was added to a solution of **1a** (1.08 mmol) in dichloromethane (25 mL) under an atmosphere of argon. The mixture was stirred for 24 h at room temperature, covered with aluminum foil, and then filtered through celite to remove the formed AgBr. $[RuCl_2(p\text{-cymene})]_2$ (0.43 mmol) was added to the colorless solution, and the reaction mixture was stirred for 24 h at room temperature. The resulting mixture was filtered through celite, and the solvent was removed under vacuum to afford the product. The crude product was recrystallized from dichloromethane:diethyl ether (1:2) at room temperature. The orange-brown crystals were filtered off, washed with diethyl ether (3 × 10 mL) and dried under vacuum. Yield: 78%. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.22 [d, 6H, $J$ = 8 Hz, (C$H_3$)$_2$CHC$_6$H$_4$CH$_3$-*p*], 1.62 [s, 3H, $H_{Ad}$], 1.77 [q, 6H, $J$ = 8 Hz, $H_{Ad}$], 1.89 [s, 6H, $H_{Ad}$], 2.06 [s, 3H (CH$_3$)$_2$CHC$_6$H$_4$C$H_3$-*p*], 2.91 [hept, 1H, $J$ = 8 Hz, (CH$_3$)$_2$C$H$C$_6$H$_4$CH$_3$-*p*], 4.06 [s, 3H, NC$H_3$], 5.30–5.58 [m, 4H, (CH$_3$)$_2$CHC$_6$$H_4$CH$_3$-*p*], 5.64 [s, 2H, C$H_2$C$_6$H$_4$Ad], 6.87 [d, 1H, $J$ = 4 Hz, NC$H$CHN], 6.98 [d, 1H, $J$ = 4 Hz, NCHC$H$N], 7.19 [d, 2H, $J$ = 8 Hz, $CH_2C_6H_4$Ad], 7.34 [d, 2H, $J$ = 8 Hz, $CH_2C_6H_4$Ad]. $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 18.7, 28.9, 30.8 [(C$H_3$)$_2$C$H$C$_6$H$_4$C$H_3$-*p*], 36.1, 36.7, 39.8 [$C_{Ad}$], 43.2 [NC$H_3$], 54.7 [$CH_2C_6H_4$Ad], 98.9, 108.4, 123.1, 125.3, 127.3, 134.6, 151.2 [$CH_2C_6H_4$Ad and (CH$_3$)$_2$CHC$_6$H$_4$CH$_3$-*p*], 123.7 [NCHCHN], 174.4 [Ru-$C_{carb}$]. Anal. Calc. for $C_{31}H_{40}N_2RuCI_2$: C, 47.59; H, 4.99; N, 3.47. Found: C, 47.41; H,4.83; N, 3.59%.

#### 4.3.4. Dichloro-[1-(4-Adamantylbenzyl)-3-(3,5-dimethylbenzyl)-5,6-dimethylbenzimidazol-2-ylidene](p-cymene) ruthenium(II), **2b**

Yield: 70%. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.13 [d, 6H, $J$ = 8 Hz (C$H_3$)$_2$CHC$_6$H$_4$CH$_3$-*p*], 1.60–1.80 [m, 12H, $H_{Ad}$], 1.90 [s, 3H (CH$_3$)$_2$CHC$_6$H$_4$C$H_3$-*p*], 2.09 [s, 9H, $H_{Ad}$ and $CH_2C_6H_3$(C$H_3$)$_2$–3,5], 2.21 [s, 3H, C$_6$H$_3$(C$H_3$)$_2$–5,6], 2.31 [s, 3H, C$_6$H$_2$(C$H_3$)$_2$–5,6] 2.58 [hept, 1H, $J$ = 4 Hz, (CH$_3$)$_2$C$H$C$_6$H$_4$CH$_3$-*p*], 4.99–5.27 [m, 4H, (CH$_3$)$_2$CHC$_6$$H_4$CH$_3$-*p*], 5.58–5.64 [m, 2H, C$H_2$C$_6$H$_3$(CH$_3$)$_2$–3,5], 6.50–6.56 [m, 2H, C$H_2$C$_6$H$_4$Ad], 6.61[s, 2H, $CH_2C_6H_3$(CH$_3$)$_2$–3,5], 6.84 [s, 2H, C$_6$$H_2$(CH$_3$)$_2$–5,6], 6.92[s, 2H, $CH_2C_6H_3$(CH$_3$)$_2$–3,5], 7.04 [d, 2H, $J$ = 8 Hz, $CH_2C_6H_4$Ad], 7.33 [d, 2H, $J$ = 8 Hz, $CH_2C_6H_4$Ad]. $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 17.9, 20.2, 21.5 [(C$H_3$)$_2$C$H$C$_6$H$_4$C$H_3$-*p*], 28.9 [$CH_2C_6H_3$(C$H_3$)$_2$–3,5], 30.4, 36.1, 36.7 [$C_{Ad}$], 43.2 [$CH_2C_6H_3$(C$H_3$)$_2$–3,5], 52.1, [$CH_2C_6H_3$(C$H_3$)$_2$–3,5], 52.2 [NC$H_2$Ar], 96.9, 106.9, 111.7, 123.5, 125.5, 128.9, 132.2, 134.4, 135.0, 138.1, 150.6 [C$_6$H$_2$(CH$_3$)$_2$–5,6, $CH_2C_6H_3$(CH$_3$)$_2$–3,5, $CH_2C_6H_4$Ad and (CH$_3$)$_2$CHC$_6$H$_4$CH$_3$-*p*], 189.0 [Ru-$C_{carb}$]. Anal. Calc. for $C_{45}H_{54}N_2RuCI_2$: C, 55.82; H, 5.50; N, 2.83. Found: C, 55.79; H, 5.58; N, 2.97%.

#### 4.3.5. Dichloro-[1-(4-Adamantylbenzyl)-3-(4-tert-butylbenzyl) benzimidazol-2-ylidene](p-cymene) ruthenium(II), **2c**

Yield: 76%. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.14 [d, 6H $J$ = 4 Hz (C$H_3$)$_2$CHC$_6$H$_4$CH$_3$-*p*], 1.31 [s, 12H, $H_{Ad}$], 1.31 [s, 9H, $CH_2C_6H_4$(C$H_3$)$_3$], 1.77 [d, 6H, $J$ = 8 Hz, $CH_2C_6H_4$C(C$H_3$)$_3$], 1.89 [s, 3H (CH$_3$)$_2$CHC$_6$H$_4$C$H_3$-*p*], 2.77 [hept, 1H, $J$ = 4 Hz, (CH$_3$)$_2$C$H$C$_6$H$_4$CH$_3$-*p*], 5.07 and 5.35 [s, 4H, (CH$_3$)$_2$CHC$_6$$H_4$CH$_3$-*p*], 6.59–7.38 [m, 16H, $CH_2C_6H_4$Ad, C$H_2$C$_6$H$_4$Ad, C$_6$$H_4$, $CH_2C_6H_4$C(CH$_3$)$_3$ and C$H_2$C$_6$H$_4$C (CH$_3$)$_3$]. $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 18.2, 22.9, 28.8 [(C$H_3$)$_2$C$H$C$_6$H$_4$C$H_3$-*p*], 31.4, 34.6, 36.1 [$CH_2C_6H_3$(C$H_3$)$_3$], 36.7, 43.1, 43.2 [$C_{Ad}$], 52.6 [NC$H_2$Ar], 84.6, 85.5, 97.3, 107.2, 111.8, 122.1, 125.4,134.4, 135.6, 150.7 [C$_6$H$_4$, $CH_2C_6H_4$C(CH$_3$)$_3$, $CH_2C_6H_4$Ad and (CH$_3$)$_2$CHC$_6$H$_4$CH$_3$-*p*], 191.4 [Ru-$C_{carb}$]. Anal. Calc. for $C_{45}H_{54}N_2RuCI_2$: C, 55.82; H,5.50; N, 2.83. Found: C, 55.79; H, 5.62; N, 2.98%.

#### 4.3.6. Dichloro-[1-(4-adamantylbenzyl)-3-(2,3,4,5,6-pentamethylbenzyl) benzimidazol-2-ylidene](p-cymene) ruthenium(II), **2d**

Yield: 72%. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.25 [m, 6H (C$H_3$)$_2$CHC$_6$H$_4$CH$_3$-*p*], 1.58 [s, 6H, $H_{Ad}$], 1.76 [d, 6H, $J$ = 16 Hz, $H_{Ad}$], 1.89 [s, 3H (CH$_3$)$_2$CHC$_6$H$_4$C$H_3$-*p*], 1.89, 2.07, 2.32 [s, 15H, $CH_2C_6$(C$H_3$)$_5$], 2.83 [hept, 1H, $J$ = 4 Hz, (CH$_3$)$_2$C$H$C$_6$H$_4$CH$_3$-*p*], 5.26–5.58 [m, 4H, (CH$_3$)$_2$CHC$_6$$H_4$CH$_3$-*p*], 6.19–7.32 [m, 12H, $CH_2C_6H_4$Ad, C$H_2$C$_6$H$_4$Ad, C$_6$$H_4$, C$H_2$C$_6$(CH$_3$)$_5$] $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ = 15.8, 17.3, 18.4 [(C$H_3$)$_2$C$H$C$_6$H$_4$C$H_3$-*p*], 28.9, 30.9, 36.1, 36.7, 36.8 [$CH_2C_6$(C$H_3$)$_5$], 43.1, 43.2 [$C_{Ad}$], 52.6 [NC$H_2$Ar], 96.4, 106.9, 111.9, 122.5, 125.4, 126.3, 128.9, 129.3, 134.7, 135.6, 150.6 [C$_6$H$_4$, $CH_2C_6$(CH$_3$)$_5$, $CH_2C_6H_4$Ad and (CH$_3$)$_2$CHC$_6$H$_4$CH$_3$-*p*], 190.2 [Ru-$C_{carb}$]. Anal. Calc. for $C_{46}H_{56}N_2RuCI_2$: C, 56.23; H, 5.62; N, 2.79. Found: C, 56.39; H, 5.67; N, 2.93%.

## CRediT authorship contribution statement

**Emine Özge Karaca:** Investigation. **Zieneb Imene Dehimat:** Investigation. **Sedat Yaşar:** Investigation. **Nevin Gürbüz:** Investigation, Visualization. **Dahmane Tebbani:** Supervision. **Bekir Çetinkaya:** Writing - review & editing. **İsmail Özdemir:** Resources, Writing - original draft, Writing - review & editing.

## 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.2021.120294.

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