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N-alkyl-5,6-dimethylbenzimidazole-ruthenium(II) catalyzed *N*-alkylating reaction

N-alkil-5,6-dimetilbenzimidazol-rutenyum(II) katalizli *N*-alkilasyon reaksiyonu

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ABSTRACT

In this study, the new *N*-coordinated 5,6-dimethyl benzimidazole ruthenium(II) complex was synthesised. It's structure was illuminated by FT-IR, ^{1}H and ^{13}C NMR spectroscopy methods. This complex has been tested for the *N*-alkylation of aromatic amines with arylmethyl alcohols under neat conditions in the presence of KOBu^{t} under solvent-free conditions, at 120 ºC. Compound (**2**) is stable and have high selective activity for *N*-alkylation reactions of primary amines to afford secondary amines. It has been found that this complex is effective catalysts for the alkylation of aromatic amines with various alcohols without using solvent. In order to determine the optimum conditions of the catalytic system, **2** catalyzed *N*-alkylation of aniline with benzyl alcohol was performed as a model reaction. The results showed that the optimum conditions were achieved with 0.025 mmol of catalyst in a solvent-free environment. After that the reactions were performed at a molar ratio of 1:0.025:1 aniline / catalyst / base (S / C / base). It was observed that the catalyst **2** was very active in the reactions using 2-pyridyl amine. Although the conversion is relatively good in reactions using aniline, it was observed that the conversion and yield were quite low in the reactions using 2,4-dimethyl aniline.

Keywords: amine, hydrogen auto-transfer method, *N*-alkylation, ruthenium

ÖZET

Bu çalışmada, yeni *N*-koordine 5,6-dimetil benzimidazol rutenyum (II) kompleksi sentezlendi. Yapısı FT-IR, ^{1}H ve ^{13}C NMR spektroskopi yöntemleriyle aydınlatıldı. Bu kompleks, çözücüsüz ortamda, aromatik aminlerin çeşitli alkollerle, 120 °C'de KOBu^{t} varlığında *N*-alkilasyonu için test edilmiştir. Bileşik (**2**) havaya ve neme karşı kararlıdır. Ayrıca ikincil aminleri elde etmek için birincil aminlerin *N*-alkilasyon reaksiyonları için yüksek seçiciliğe sahiptir. Aromatik aminlerin çeşitli alkoller ile çözücü kullanmadan alkilasyonu için etkili katalizör olduğu da bulunmuştur. Çalışma kapsamında öncelikle, katalitik sistemin optimum koşullarını belirlemek için, model reaksiyon olarak kompleks **2** ile katalizlenmiş anilinin benzil alkol ile *N*-alkilasyonu reaksiyonu gerçekleştirildi. Sonuçlar, çözücü içermeyen bir ortamda 0.025 mmol katalizör ile optimum koşulların karşılandığını gösterdi. Reaksiyonlar, 1: 0.025: 1; anilin / katalizör / baz (S / C / baz) molar oranında gerçekleştirildi. Katalizör 2, substrat olarak 2-pridil aminin kullanıldığı tepkimelerde oldukça aktif olduğu gözlendi. Anilinin kullanıldığı tepkimelerde dönüşüm nispeten iyi olmasına rağmen, 2,4-dimetil anilinin kullanıldığı tepkimelerde dönüşüm ve seçiciliğin oldukça düşük olduğu gözlendi.

Anahtar Kelimeler: amin, hidrojen oto-transfer yöntemi, *N*-alkilasyon, rutenyum

1. INTRODUCTION

Because of their notable biological activities, azole derivatives are commonly applied to the synthesis of pesticides and medicines. In the field of coordinated functional materials, azoles are often used where they serve as good electron donors and also have poor interactions and have become effective ligands for transition-metal catalysts because of their air and moisture stability.

Contemporary interest in the coordination chemistry of metal derivatives containing azole ligands has been growing. Such compounds are mixed with NHC-metal complexes and *N*-coordinate metal complexes and these compounds are used in various catalytic systems such as C-C bond formation reactions, olefin metathesis, hydrosilylation, hyrdroformilation, transfer hydrogenation, polymerization reactions and *N*-alkylation reactions.

The synthesis methods of amine compounds have been the subject of extensive research since amine compounds have an important biological, medical, agricultural, dye and polymer chemistry in organic chemistry (Ricci, 2008; Lawrence, 2006). Amines are synthesised by conventional methods such as hydroamination of alkyne alkanes, amination of aryl halides, reductive amination with carbonyl complexes and *N*-alkylation with alkyl halides. These methods have disadvantages such as the use of environmentally harmful halide derivatives, the use of expensive amines as starting material, the formation of waste salts in excess, and the low selectivity (Mizuno, 2009).

The hydrogen auto-transfer method used in the synthesis of amines has been carried out atmospheric pressures and without special mechanisms, since it does not require additional hydrogen. This method, known as auto transfer or self-hydrogen supply systems, requires milder conditions than conventional methods (Kim, 2019). When it comes to selectivity, cost, efficiency and environmental considerations, it has many advantages over conventional methods. In the alkylation of amines by the hydrogen auto-transfer method, only water comes out as a by-product (Shibata, 2013). Waste materials have low molecular weight, making the method unrivaled in terms of the atom effect. All these features make this method suitable for environmentally friendly and green chemistry. It is important from both industrial and academic point of view to improve selectivity and productivity by developing new and effective catalysts. Transition metal-catalyzed *N*-alkylation was first performed by Grigg (Grigg, 1981) and Watanable (Watanable, 1981). Later, many complexes of Ru, Ir, Fe, Co, Mn, Cu, Pd containing different ligands were used in this catalytic system (Elangovan, 2016; Fernandes, 2017; Kang, 2012; Mamidala, 2017; Mastalir, 2016a; Mastalir, 2016b; Pan, 2013; Prakash, 2015; Ramachandran, 2018). In the alkylation of amines by the hydrogen auto-transfer method, Ru (Yu, 2017) and Ir (Bartoszewicz, 2012) complexes are mostly used.

Many transition-metal complexes have been used as catalysts in alkylation reactions of amines with alcohols. Ruthenium complexes have been widely used in organic synthesis as the first example of transition-metal catalysts. Many ruthenium derivatives are excellent catalysts for the *N*-alkylation of amines by the homogeneous hydrogen transfer method. Our team mostly works on NHC ligands and *N*-coordinated azole ligands and their complexes and the use of these complexes in various catalytic systems. Compared to other catalysts, ruthenium complexes containing *N*-coordinated benzimidazole ligands can be synthesised more easily with high yields. When the literature is examined, the use of such complexes as catalysts in the *N*-alkylation reaction is limited. Based on the above information, a novel *N*-coordinated ruthenium complex was synthesized, characterized by FT-IR, ^{1}H and ^{13}C NMR spectroscopy and its catalytic activity under solvent-free conditions was investigated.

2. RESULTS AND DISCUSSIONS

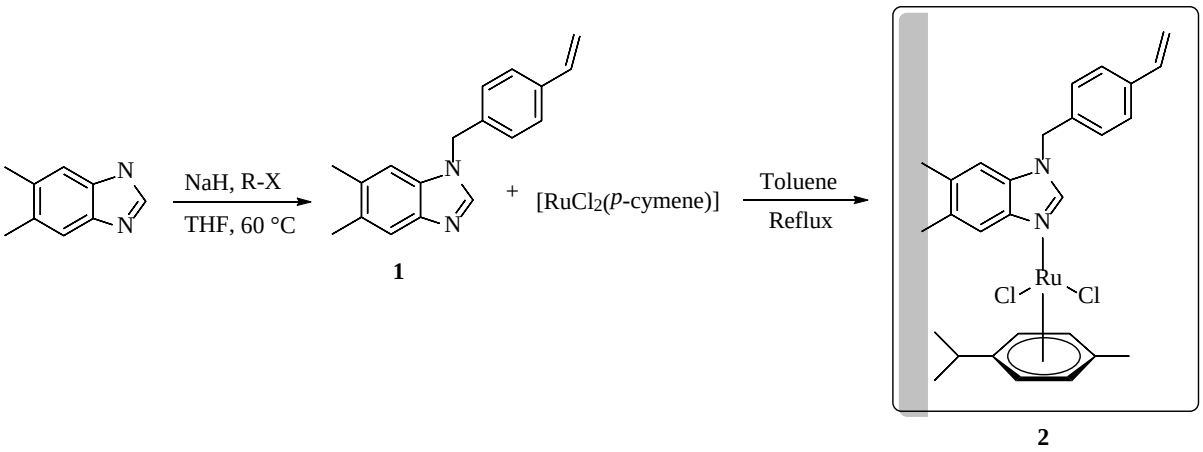
2.1.Preparation of 1-(4-vinylbenzyl)5,6-dimethylbenzimidazole, 1

5,6-Dimethylbenzimidazole and NaH stirred at THF for one hour and 4-vinylbenzyl chloride was added dropwise and heated. Then 1-(4-vinylbenzyl)5,6-dimethylbenzimidazole (1) was obtained nearly quantitative yield, 84 %. The compound **1** is stable to air and moisture. It was soluble in DMSO. The NC*H*N proton appear in the ^{1}H NMR at 7.83. The experimental findings are in line with the literature (Boztepe, 2019).

2.2.Preparation of ruthenium complex, 2

The solution of 1-(4-vinylbenzyl)5,6-dimethylbenzimidazole and $[RuCl_2(p\text{-cymene})]_2$ of toluene was heated. Upon cooling to room temperature, a solid orange of **2** was obtained nearly quantitative yield, 78 %. The compound **2** is stable to air and moisture. It was soluble in $CDCl_3$. The NC*H*N

proton appear in the ^{1}H NMR at 8.44. The experimental findings are in line with the literature (Şahin, 2019).



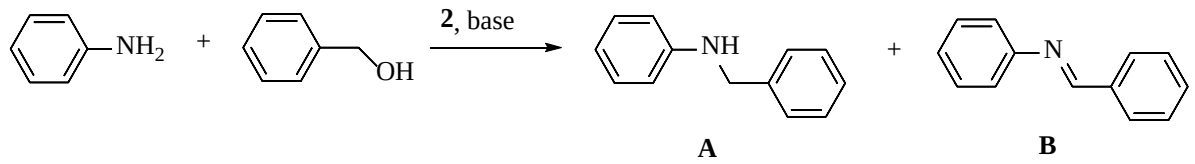
Scheme 1. Synthesis of ruthenium complex.

2.3.The *N*-alkylation of amines with alcohols

Since amine compounds have an important field in organic chemistry such as biological, medical, agricultural, dye and polymer chemistry, the synthesis methods of these compounds have been a subject of extensive research. Amines are synthesised by classical methods such as hydroamination of alkyne or alkenes, amination of aryl halides, reductive amination with carbonyl complexes and N-Alkination with alkyl halides. These environmental methods have disadvantages such as the encryption of halide derivatives harmful to amines as starting materials, the formation of excess screen waste salt, and low selectivity. Therefore, effective and environmentally friendly catalytic processes are of great importance.

Since the hydrogen autotransfer method used in amine synthesis lately does not contain additional hydrogen, it is carried out in the atmosphere and without using special equipment. This method, known as autotransfer or stylized, makes more moderate sense than the methods. Selectivity, efficiency and environmental conditions have many advantages over conventional methods (Bähn, 2011).

In order to determine the optimum conditions of the catalytic system, **2** catalyzed *N*-alkylation of aniline with benzyl alcohol was performed as a model reaction (Scheme 2). Control experiments were conducted with a ruthenium catalyst to see the role of the base in the catalytic system (Yiğit, 2020). The expected yield from the reaction in the absence of the base could not be obtained. After that, to find the best of the base, various bases have been tried such as KOH, K_2CO_3, Cs_2CO_3 and $KOBu^t$. In some other cases it is seen that when imine is formed next to the amine, this indicates that hydrogen transfer has not occurred. Furthermore, increasing the reaction temperature from 100 °C to 120 °C and increasing the amount of catalyst allowed the reaction to be completed with 91% amine formation. When the reaction was carried out at 120 °C with $KOBu^t$, the amount of catalyst and the solvent were tested. The results showed us that the optimum conditions were met with 0.025 mmol of catalyst in a solvent-free environment. After the optimum conditions were determined, they were used in the same reaction for other complexes.



Scheme 2. Optimization studies of *N*-alkylation reaction of aniline with benzyl alcohol catalyzed by complex **2**.

In a standard experiment, KOBu^t (0.01 mmol), aromatic amine (1 mmol), alcohol derivative (1.5 mmol), and Ru-azole complex **2** (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, CH_2Cl_2 (2 mL) was added, and filtered through a short SiO_2 pad. The filtrate was analyzed by GC. The yields were based on the corresponding aniline. The reactions were performed at a molar ratio of 1:0.025:1 aniline / catalyst / base (S / C / base). It is worth noting that when the excess of benzyl alcohol (5 mmol) is used, the only secondary amine is formed in the catalytic reaction.

The *N*-alkylation of aniline with different alcohols (benzyl alcohol, *p*-methoxybenzyl alcohol, *p*-methybenzyl alcohol, 3,4-dimethoxybenzyl alcohol and furfuryl alcohol) was investigated using **2** catalysts to obtain the secondary amines under mild reaction conditions (Figure 1). When the reaction results using aniline as a substrate were examined, it was observed that although the conversions were close to high, selectivity was quite high. The corresponding amines were obtained with high selectivity.

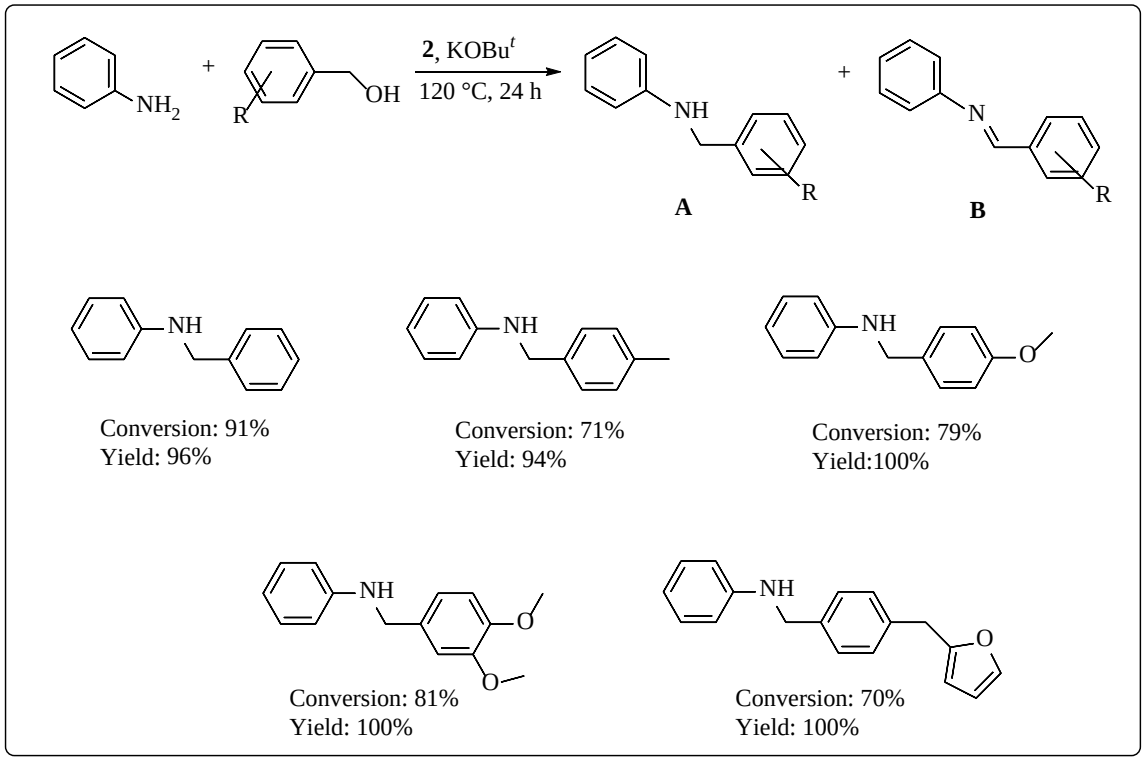


Figure 1. *N*-alkylation of aniline with alcohols

Then it was observed what the result would be when using a sterically hindered aniline derivative. In the next step of the same reaction, 2,4-dimethyl aniline was used as substrate. The *N*-alkylation of 2,4-dimethyl aniline with different alcohols (benzyl alcohol, *p*-methoxybenzyl alcohol, *p*-methybenzyl alcohol, 3,4-dimethoxybenzyl alcohol and furfuryl alcohol) was investigated using **2**

catalysts to obtain the secondary amines under mild reaction conditions (Figure 2). When the results were examined, it was observed that the transformations in the reactions using 2,4-dimethyl aniline were very low. The selectivity was observed to be 100% when only *p*-methyl benzyl alcohol and furfuryl alcohol were used. It was quite low in selectivity for other alcohols.

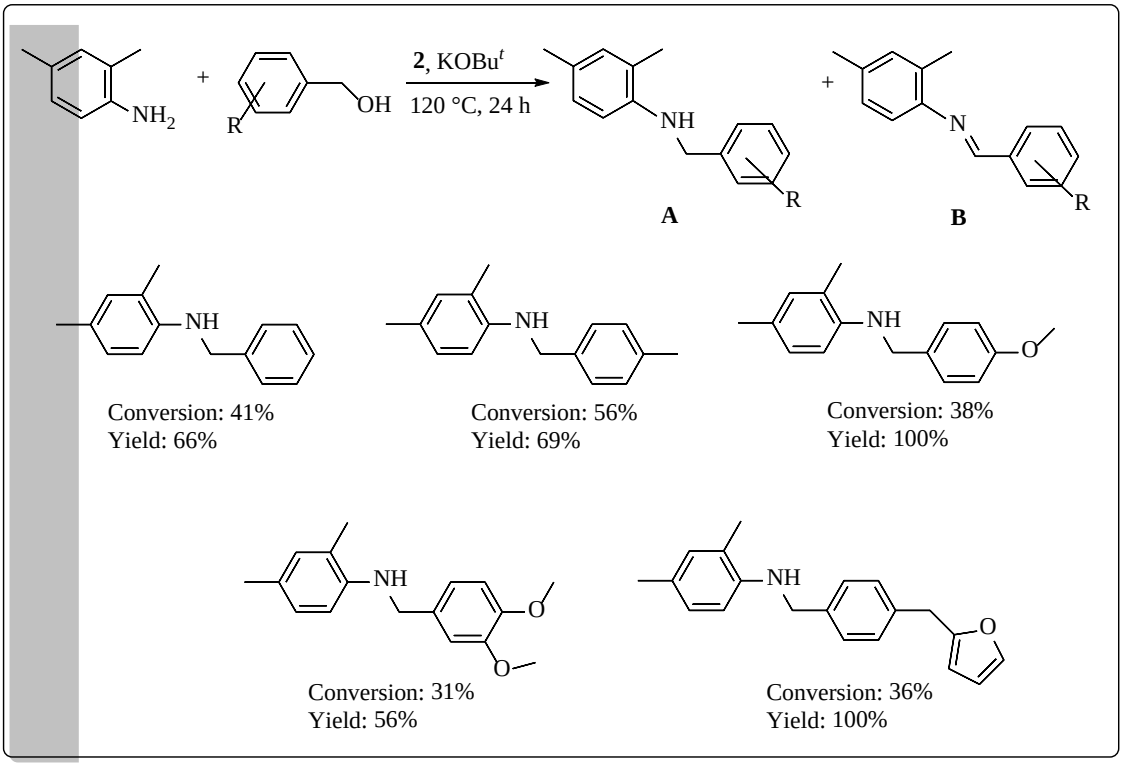


Figure 2. *N*-alkylation of 2,4-dimethylaniline with alcohols

Finally, the results were checked to see what would happen if a heteroatom containing compound was used as a substrate. In this, 2-pyridyl amine was used as substrate. The *N*-alkylation of 2-aminopyridine with the same alcohols (benzyl alcohol, *p*-methoxybenzyl alcohol, *p*-methybenzyl alcohol, 3,4-dimethoxybenzyl alcohol and furfuryl alcohol)) was also investigated by using **2** catalysts to obtain *N*-alkylated amines under the same conditions (Figure 3). 2-(*N*-Alkylamino)pyridines were obtained in good to excellent selectivity in the presence of 2,5 mol% catalysts. Also, under these catalytic conditions, the heteroaromatic moiety in 2-aminopyridine has also been well tolerated.

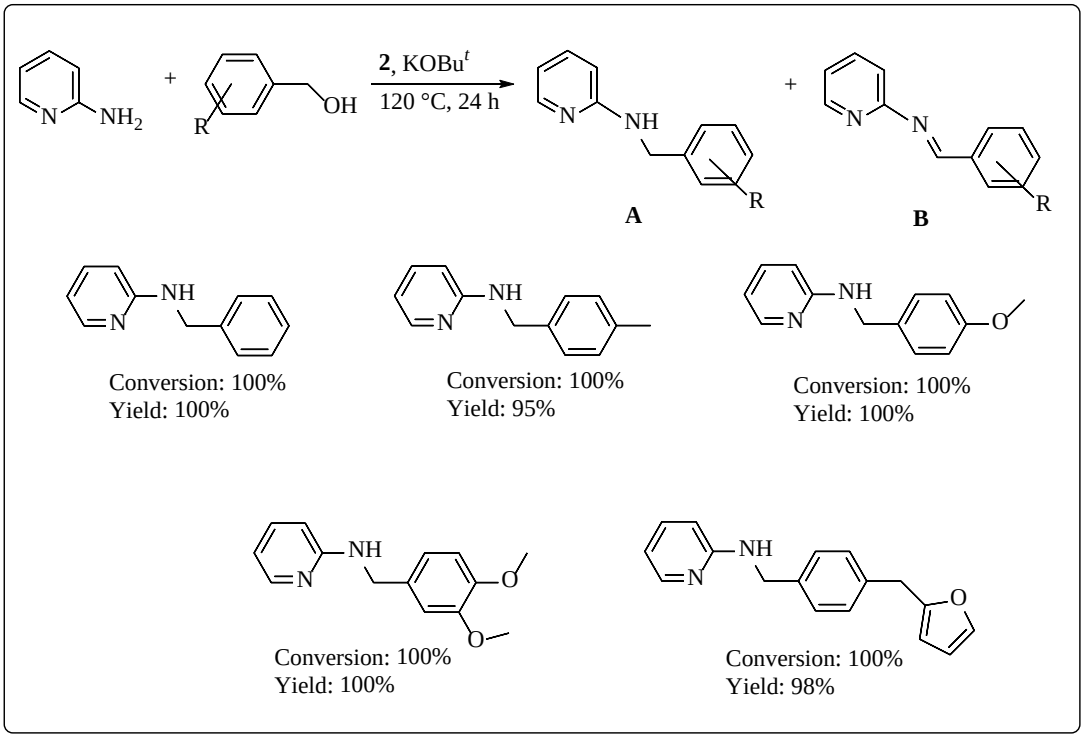


Figure 3. *N*-alkylation of 2-pyridyl amine with alcohols.

3. EXPERIMENTAL SECTION

3.1.Materials

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

3.2.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 Varian As 300 Merkur spectrometer operating at 300 MHz (^{1}H), 75 MHz (^{13}C) in $CDCl_3$ and DMSO-d6 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 (δ = 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. 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 30m 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.

3.3.Synthesis

3.3.1. Synthesis of 1-(4-vinylbenzyl)5,6-dimethylbenzimidazole

5,6-Dimethylbenzimidazole (10 mmol) was applied to the NaH (10 mmol) solution in dry THF (30 mL), at room temperature for 1 h and 4-vinylbenzyl chloride (10.1 mmol) was added dropwise and heated at 60 ºC for 24 h. The THF was then removed under the vacuum. Dichloromethane (50 mL) was applied to the solid. The mixture was filtered and the solution obtained was concentrated under vacuum. The solution was then distilled and 1-(4-vinylbenzyl)5,6-dimethylbenzimidazole (1) was obtained. Yield: 84 %. mp: 109-110 °C. FT-IR $\nu_{(CN)}$: 1614 cm^{-1}; ^{1}H NMR (399.9 MHz, DMSO-d6, 25 °C): δ = 2.34 (d, 6H, *J* = 12, 5,6-(C*H*$_3$)$_2$-C$_6$H$_2$), 5.26 (d, 1H, *J* = 12, NCH$_2$C$_6$H$_4$CH=C*H*$_2$-4), 5.29 (s, 2H, NC*H*$_2$C$_6$H$_4$CH=CH$_2$-4), 5.73 (d, 1H, *J* = 12, NCH$_2$C$_6$H$_4$CH=C*H*$_2$-4), 6.68 (q, 1H, NCH$_2$C$_6$H$_4$C*H*=CH$_2$-4), 7.04 and 7.58 (s, 2H, *J* = 8, 5,6-(CH$_3$)$_2$-C$_6$*H*$_2$), 7.11 and 7.36 (d, 4H, *J* = 8,

$NCH_2C_6H_4CH=CH_2$-4), 7.83 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, DMSO-d6, 25 °C): δ= 20.2, 20.5, 41.0, 48.4, 110.0, 113.8, 114.5, 120.4, 126.2, 126.7, 127.1, 128, 131.1, 132.2, 132.4, 135.2, 136.0, 136.5, 137.4, 142.4, 142.5.

3.3.2. Dichloro-[1-(4-vinylbenzyl)5,6-dimethylbenzimidazole]-(p-cymene) ruthenium (II)

The solution of 1-(4-vinylbenzyl)5,6-dimethylbenzimidazole (1,0 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0,5 mmol) in 10 mL of toluene was heated under reflux for 4 h. Upon cooling to room temperature, a solid orange of 2 was obtained. The solid (2) was filtered and washed with diethyl ether (3x10 mL) and washed under vacuum. The crude product has been crystallized in CH_2Cl_2/Et_2O. Yield: 78 %. mp: 167-168 °C. FT-IR $\nu_{(CN)}$: 1462 cm^{-1}; ^{1}H NMR (399.9 MHz, $CDCl_3$, 25 °C): δ = 1.22 [d, 6H, *J* = 4, $(CH_3)_2CHC_6H_4CH_3$-*p*], 2.14 [s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*], 2.32 (s, 6H, 5,6-$(CH_3)_2$-C_6H_2), 2.39 (s, 6H, 5,6-$(CH_3)_2$-C_6H_2), 2.80 [h, 1H, $(CH_3)_2CHC_6H_4CH_3$-*p*], 5.23 (s, 2H, $NCH_2C_6H_4CH=CH_2$-4), 5.27 (d, 1H, *J* = 4, $NCH_2C_6H_4CH=CH_2$-4), 5.38 and 5.52 [d, 4H, *J* = 4, $(CH_3)_2CHC_6H_4CH_3$-*p*], 5.74 (d, 1H, *J* = 4, $NCH_2C_6H_4CH=CH_2$-4), 6.69 (q, 1H, *J* = 4, $NCH_2C_6H_4CH=CH_2$-4), 7.05 and 7.76 (s, 2H, *J* = 8, 5,6-$(CH_3)_2$-C_6H_2), 7.14 and 7.37 (d, 4H, *J* = 8, $NCH_2C_6H_4CH=CH_2$-4), 8.44 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ= 18.5, 20.5, 20.7, 22.3, 30.6, 49.2, 97.7, 102.4, 110.9, 114.8, 120.4, 125.4, 126.8, 127.3, 128.3, 129.0, 132.6, 132.7, 133.8, 134.2, 135.9, 137.7, 141.3, 141.6, 143.9.

3.3.3. General procedure for the N-alkylation of aniline with alcohols

Under the optimized reaction conditions, in a Schlenk tube, a mixture of aniline derivative (1.0 mmol), excess of alcohol derivative (1.5 mmol), KOBut (1.0 mmol) and Ru catalyst (2) (0.025 mmol, 2.5 mol %) was stirred at 120 °C for 24 h under argon atmosphere. After cooling to room temperature, CH_2Cl_2 (2 ml) was added to the crude mixture. The obtained mixture was passed through a pad of short silica gel and the filtrate was analyzed by GC.

4. CONCLUSION

In conclusion, new coordinated ruthenium(II) complex was prepared from 1-(4-vinylbenzyl)5,6-dimethylbenzimidazole. It has been found that the newly prepared complex is stable against air and moisture. The catalytic activity of the resulting Ru(II) complexes was evaluated in the alkylation of aniline derivatives via different alcohols. It was observed that the selectivity was high in reactions using aniline as a substrate. However, the selectivity wasn't very high. It was observed that the conversation was low in the reactions where 2,4-dimethyl aniline was used as a substrate. Nevertheless, it was seen that the selectivity was better.

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