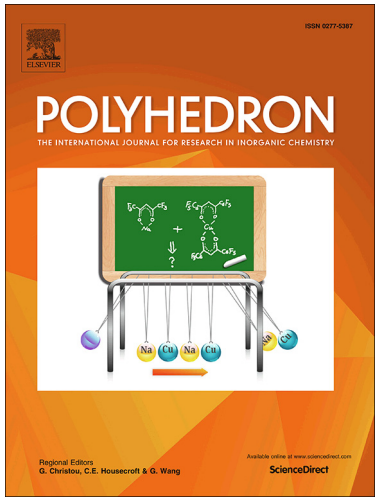

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Active ruthenium(II)-NHC complexes for alkylation of amines with alcohols using solvent-free conditions

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Abstract

A series of new ruthenium(II) complexes bearing *N*-heterocyclic carbene ligands with benzylic groups were prepared by transmetallation reactions between silver(I) *N*-heterocyclic carbene complexes and $[RuCl_2(p\text{-cymene})]_2$. All of the obtained complexes were characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy, and the molecular structure of compound **3c** was also determined by X-ray crystallography. These ruthenium complexes were tested for the alkylation of aromatic amines with a wide range of primary alcohols under solvent-free conditions using the hydrogen borrowing strategy. All of the compounds tested here showed excellent catalytic activity for these reactions and *N*-monoalkylated products were obtained selectively using 2.5 mol % of the ruthenium complexes.

Keywords: Ru-*N*-Heterocyclic carbene complex, X-ray crystallography, Borrowing hydrogenation reaction, Alkylation of amine.

1. Introduction

The borrowing hydrogen methodology, also called hydrogen auto-transfer, is an attractive method for the formation of carbon-carbon and carbon-heteroatom bonds in the presence of transition metal catalysts and has received much attention as greener process in recent years [1]. This process involves three steps, but it is carried out in one pot. In the initial step, hydrogen is temporarily removed from an alcohol with a transition metal catalyst to form a carbonyl compound, then the carbonyl compound reacts with a nucleophile to form an unsaturated intermediate. In the last step, the unsaturated intermediate is reduced by the metal

hydride complex to obtain the final product. This methodology has atom efficiency and a low environmental impact, in addition to operational simplicity [2], and permits to the alkylation of many different compounds, such as amines, ketones, secondary alcohols, thiols, amides and nitriles, using alcohols [3]. Alcohols as alkylating agents are readily available, relatively cheap and less toxic than the corresponding alkyl halide, and water is the only by-product in the overall process. Instead of alcohols, amines can also be used as the source of electrophiles in this process, but the use of amines is very limited [4]. The alkylation of amines with alcohols using transition metal catalysts as an alternative to conventional alkylation procedures is an environmentally benign procedure to produce alkylated amines, which are widely used as biologically active compounds, agrochemicals, functionalized materials and dyes in both the bulk and fine chemical industries [5]. Alkylated amines are usually prepared by the alkylation of amines with alkyl halides [6] or by reductive amination of carbonyl compounds with amines using stoichiometric reducing agents [7]. However, these reactions have significant drawbacks, such as toxicity of the alkylating and reducing agents, the formation of large amounts of waste, acidic reaction conditions and unwanted side products. Numerous catalytic methods, such as Buchwald-Hartwig amination [8], hydroamination [9], and hydroaminomethylation [10] and the borrowing hydrogen methodology [11], have been developed for the purpose of overcoming these issues. In 1981, Grigg [12] and Watanabe [13] independently reported the first examples of the alkylation of amines with alcohols using homogeneous catalysts by the borrowing hydrogen method. In these reports, $RhH(PPh_3)_4$ and $RuCl_2(PPh_3)_3$ complexes were used as a catalyst for the alkylation of amines. Since then, a number of homogeneous transition metal-based catalytic systems have been developed for alkylation of amines with alcohols [14]. Heterogeneous catalysts have also been explored for this type of transformation [15], but some of them suffer from drawbacks such as low selectivity and activity for mono-alkylation, and the need for high temperature and additives or co-catalysts. In addition, biocatalysts [16] and chiral catalysts [17] have been applied for the amination of alcohols to prepare enantiopure amines, which are key intermediates for the synthesis of organic compounds in the fine chemicals and pharmaceutical industries. In recent years, studies have been focused on the development of more efficient catalysts for performing *N*-alkylation reactions under mild conditions. Especially, catalytic systems based on iridium provide mild conditions for the *N*-alkylation of amines. For example, Martin-Matute and co-workers [18] reported the alkylation of amines with alcohols using Cp*Ir(NHC) complexes under base-free conditions with short reaction times. High yields were also obtained at low temperature, but long reaction times were required. Li and

Andersson [19] demonstrated that a bidentate Ir(NHC-phosphine) complex catalyzed the *N*-monoalkylation of aromatic amines with primary alcohols at room temperature and under solvent-free conditions. Fernandes and Royo [20] recently described the use of $IrCl_2Cp^*$(NHC) complexes as a catalyst for the *N*-alkylation of amines with alcohols in water under base-free conditions. In addition to iridium-NHC complexes [21], ruthenium complexes [22] are also highly active for the *N*-alkylation of amines under mild conditions. Enyong and Moasser [23] achieved the alkylation of primary and secondary amines with alcohols at low or room temperature using $[RuCl_2(p\text{-cymene})]_2$/amino amide ligand catalyst systems. Many protocols for the *N*-alkylation of amines have been reported that require the use of organic solvents and long reaction times. Herein, we wish to report the synthesis and characterization of new *p*-cymene-ruthenium(II)-NHC complexes and their use as catalysts for the *N*-alkylation reactions of aniline with arylmethyl alcohols under solvent-free conditions.

2. Experimental

2.1. Materials and methods

All reactions for the preparation of the ruthenium(II)-NHC complexes were carried out under argon in flame-dried glassware using standard Schlenk techniques. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). All reagents were purchased from Sigma-Aldrich, Merck, and Fluka. $[RuCl_2(p\text{-cymene})]_2$ [24], perhydrobenzimidazolium salts [25,26] and the Ag-NHC complexes [27,28] were synthesized according to published procedures. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance III Merkur spectrometer operating at 400 MHz (^1H) and 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. Coupling constants (*J* values) are given in Hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept = septet and m = multiplet signal. FT-IR spectra were recorded on ATR unit in the range 400-4000 cm^{-1} on a Perkin Elmer Spectrum 100. GC was measured by a Shimadzu GC-2010 Plus gas chromatograph equipped with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected.

The X-ray single crystal diffraction data were recorded on a Bruker APEX-II CCD diffractometer. A suitable crystal was selected, coated with Paratone oil and mounted onto a Nylon loop on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 296(2) K during the data collection. The data were collected with MoKα (λ = 0.71073 Å) radiation for

complex **3c** at a crystal-to-detector distance of 40 mm. Using Olex2 [29], the structure was solved with the Superflip [30-32] structure solution program, using the Charge Flipping solution method and refined by full-matrix least-squares techniques on F^2 using ShelXL [33] with refinement of F^2 against all reflections. Hydrogen atoms were constrained by difference maps and were refined isotropically and all non-hydrogen atoms were refined anisotropically. The molecular structure plots were prepared using PLATON [34].

2.2. Synthesis of the perhydrobenzimidazolium salts, 1

The perhydrobenzimidazolium salts, **1**, were synthesized according to the literature [28].

2.3. Synthesis of the silver(I)-NHC complexes, 2

The silver(I)-NHC complexes, **2**, were synthesized according to literature [28].

2.4. Synthesis of the ruthenium(II)-NHC complexes, 3

A solution of the required silver(I)-NHC complex (0.86 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.43 mmol) in dichloromethane (20 mL) was stirred for 24 h at room temperature in the dark. The resulting mixture was then 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 thus obtained were filtered off, washed with diethyl ether (3 x 10 mL) and dried under vacuum.

2.4.1.Dichloro-[1,3-bis(4-methylbenzyl)perhydrobenzimidazol -2-ylidene](*p*-cymene) ruthenium(II), 3a

Yield: 0.42 g, 76%, m.p.: 210 °C. IR, υ, cm^{-1}: 1513 (NCN). ^{1}H NMR ($CDCl_3$) δ, ppm: 0.90-1.10 (m, 4H, $NCHCH_2C\mathit{H}_2C\mathit{H}_2CH_2CHN$); 1.55-1.71 (m, 4H, $NCHC\mathit{H}_2CH_2CH_2C\mathit{H}_2CHN$); 3.14-3.28 (m, 2H, $NC\mathit{H}CH_2CH_2CH_2CH_2C\mathit{H}N$); 2.23 and 2.36 (s, 6H, $CH_2C_6H_4C\mathit{H}_3$-4); 5.07, 5.17, 5.30 and 5.41 (d, 4H, J = 8 Hz, $C\mathit{H}_2Ar$); 7.12, 7.19 and 7.28 (d, 8H, J = 8 Hz, $CH_2C_6\mathit{H}_4CH_3$-4); 1.19 and 1.24 (d, 6H, J = 4 Hz, *p*-$CH_3C_6H_4CH(C\mathit{H}_3)_2$); 2.06 (s, 3H, *p*-$C\mathit{H}_3C_6H_4CH(CH_3)_2$); 2.80 (sept, 1H, J = 8 Hz, *p*-$CH_3C_6H_4C\mathit{H}(CH_3)_2$); 4.66, 4.74, 5.69 and 5.75 (d, 4H, J = 16 Hz, *p*-$CH_3C_6\mathit{H}_4CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ, ppm: 23.2, 24.1, 29.4, 29.7, 54.0 and 55.4 ($NC\mathit{H}(C\mathit{H}_2)_4C\mathit{H}N$); 21.1 ($CH_2C_6H_4C\mathit{H}_3$-4); 68.1 and 69.1 ($C\mathit{H}_2Ar$); 126.2, 127.7, 128.8, 129.2, 135.1 and 136.6 ($CH_2C_6H_4CH_3$-4); 18.4 (*p*-$CH_3C_6H_4CH(C\mathit{H}_3)_2$); 21.8 (*p*-$C\mathit{H}_3C_6H_4CH(CH_3)_2$); 30.5 (*p*-$CH_3C_6H_4C\mathit{H}(CH_3)_2$); 83.4, 85.0, 85.6, 85.7, 96.9 and 107.9 (*p*-$CH_3C_6\mathit{H}_4CH(CH_3)_2$); 214.8 ($Ru\text{-}C_{carb}$).

2.4.2.Dichloro-[1,3-bis(2,4-dimethylbenzyl)perhydrobenzimidazol-2-ylidene](*p*-cymene)ruthenium(II), 3b

Yield: 0.44 g, 80%, m.p.: 223-224 °C. IR, υ, cm^{-1}: 1502 (NCN). ^1H NMR ($CDCl_3$) δ, ppm: 1.05-1.33 (m, 4H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN); 1.60-1.71 (m, 4H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN); 3.20-3.50 (m, 2H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N); 2.29, 2.30, 2.33 and 2.36 (s, 12H, CH$_2$C$_6$H$_3$(C*H*$_3$)$_2$-2,4); 4.99, 5.20, 5.24 and 5.32 (d, 4H, *J* = 8 Hz, C*H*$_2$Ar); 6.98 and 7.04 (s, 2H, CH$_2$C$_6$*H*$_3$(CH$_3$)$_2$-2,4); 7.08, 7.13, 7.29 and 7.39 (d, 4H, *J* = 8 Hz, CH$_2$C$_6$*H*$_3$(CH$_3$)$_2$-2,4); 1.09 and 1.12 (d, 6H, *J* = 4 Hz, *p*-CH$_3$C$_6$H$_4$CH(C*H*$_3$)$_2$); 1.86 (s, 3H, *p*-C*H*$_3$C$_6$H$_4$CH(CH$_3$)$_2$); 2.50-2.60 (m, 1H, *p*-CH$_3$C$_6$H$_4$C*H*(CH$_3$)$_2$); 4.20-4.30 and 5.95-6.05 (m, 4H, *p*-CH$_3$C$_6$*H*$_4$CH(CH$_3$)$_2$). ^{13}C NMR ($CDCl_3$) δ, ppm: 23.0, 24.2, 28.7, 29.5, 50.6 and 51.5 (N*C*H(*C*H$_2$)$_4$*C*HN); 19.1 and 19.3 (CH$_2$C$_6$H$_3$(*C*H$_3$)$_2$-2,4); 67.7 and 68.9 (*C*H$_2$C$_6$H$_3$(CH$_3$)$_2$-2,4); 126.2, 126.8, 131.4, 132.9, 134.8 and 136.2 (CH$_2$*C*$_6$H$_3$(CH$_3$)$_2$-2,4); 17.3 (*p*-CH$_3$C$_6$H$_4$CH(*C*H$_3$)$_2$); 21.8 (*p*-*C*H$_3$C$_6$H$_4$CH(CH$_3$)$_2$); 30.4 (*p*-CH$_3$C$_6$H$_4$*C*H(CH$_3$)$_2$); 83.9, 84.2, 85.4, 86.9, 95.8, 105.8 (*p*-CH$_3$*C*$_6$H$_4$CH(CH$_3$)$_2$); 215.2 (Ru-C_{carb}).

2.4.3. Dichloro-[1,3-bis(4-ethylbenzyl)perhydrobenzimidazol-2-ylidene](*p*-cymene) ruthenium(II), 3c

Yield: 0.44 g, 78%, m.p.: 204-205 °C. IR, υ, cm^{-1}: 1513 (NCN). ^1H NMR ($CDCl_3$) δ, ppm: 0.97-1.11 (m, 4H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN); 1.55-1.70 (m, 4H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN); 3.19-3.29 (m, 2H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N); 1.27 (t, 6H, *J* = 8 Hz, CH$_2$C$_6$H$_4$(CH$_2$C*H*$_3$)-4); 2.65 (q, 4H, *J* = 4 Hz, CH$_2$C$_6$H$_4$(C*H*$_2$CH$_3$)-4); 5.07, 5.17, 5.30 and 5.44 (d, 4H, *J* = 8 Hz, C*H*$_2$Ar); 7.14, 7.21 and 7.30 (d, 8H, *J* = 8 Hz, CH$_2$C$_6$*H*$_4$(CH$_2$CH$_3$)-4); 1.18 and 1.21 (d, 6H, *J* = 8 Hz, *p*-CH$_3$C$_6$H$_4$CH(C*H*$_3$)$_2$); 2.06 (s, 3H, *p*-C*H*$_3$C$_6$H$_4$CH(CH$_3$)$_2$); 2.78 (sept, 1H, *J* = 8 Hz, *p*-CH$_3$C$_6$H$_4$C*H*(CH$_3$)$_2$); 4.66, 4.78, 5.67 and 5.77 (d, 4H, *J* = 16 Hz, *p*-CH$_3$C$_6$*H*$_4$CH(CH$_3$)$_2$). ^{13}C NMR ($CDCl_3$) δ, ppm: 23.2, 24.1, 29.3, 29.6, 54.0 and 55.3 (N*C*H(*C*H$_2$)$_4$*C*HN); 15.5 (CH$_2$C$_6$H$_4$(CH$_2$*C*H$_3$)-4); 28.4 (CH$_2$C$_6$H$_4$(*C*H$_2$CH$_3$)-4); 68.2 and 69.0 (*C*H$_2$Ar); 126.2, 127.6, 128.0, 135.3, 136.5, 143.0 (CH$_2$*C*$_6$H$_4$(CH$_2$CH$_3$)-4); 18.4 (*p*-CH$_3$C$_6$H$_4$CH(*C*H$_3$)$_2$); 21.8 (*p*-*C*H$_3$C$_6$H$_4$CH(CH$_3$)$_2$); 30.5 (*p*-CH$_3$C$_6$H$_4$*C*H(CH$_3$)$_2$); 83.3, 84.9, 85.6, 85.8, 97.0 and 107.8 (*p*-CH$_3$*C*$_6$H$_4$CH(CH$_3$)$_2$); 214.8 (Ru-C_{carb}).

2.4.4.Dichloro-[1,3-bis(4-isopropylbenzyl)perhydrobenzimidazol-2-ylidene](*p*-cymene)ruthenium(II), 3d

Yield: 0.43 g, 72%, m.p.: 214 °C. IR, υ, cm^{-1}: 1512 (NCN). ^1H NMR ($CDCl_3$) δ, ppm: 1.01-1.30 (m, 4H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN); 1.56-1.73 (m, 4H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN); 3.16-3.29 (m, 2H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N); 1.26 (t, 12H, *J* = 8 Hz, CH$_2$C$_6$H$_4$(CH(C*H*$_3$)$_2$)-4); 2.91 (sept, 2H, *J* = 8 Hz, CH$_2$C$_6$H$_4$(C*H*(CH$_3$)$_2$)-4); 5.07, 5.16, 5.30 and 5.44 (d, 4H, *J* = 8 Hz, C*H*$_2$Ar); 7.17, 7.24 and 7.30 (d, 8H, *J* = 8 Hz,

$CH_2C_6H_4$(CH(CH_3)$_2$)-4); 1.17 and 1.22 (d, 6H, *J* = 8 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$); 2.05 (s, 3H, *p*-$CH_3C_6H_4CH(CH_3)_2$); 2.75 (sept, 1H, *J* = 8 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$); 4.66, 4.78, 5.67 and 5.77 (d, 4H, *J* = 16 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ, ppm: 23.1, 24.2, 29.3, 29.6, 54.0 and 55.2 (N*C*H(*C*H$_2$)$_4$*C*HN); 24.0 ($CH_2C_6H_4(CH(CH_3)_2)$-4); 33.7 ($CH_2C_6H_4(CH(CH_3)_2)$-4); 68.2 and 68.9 (*C*H$_2$Ar); 126.2, 126.5, 127.6, 135.4, 136.6 and 147.7 ($CH_2C_6H_4(CH(CH_3)_2)$-4); 18.4 (*p*-$CH_3C_6H_4CH(CH_3)_2$); 21.8 (*p*-$CH_3C_6H_4CH(CH_3)_2$); 30.5 (*p*-$CH_3C_6H_4CH(CH_3)_2$); 83.3, 84.7, 85.7, 85.9, 97.0 and 107.6 (*p*-$CH_3C_6H_4CH(CH_3)_2$); 214.8 (Ru-C_{carb}).

2.4.5.Dichloro-[1,3-bis(4-tert-butylbenzyl) perhydrobenzimidazol-2-ylidene](*p*-cymene) ruthenium(II), 3e

Yield: 0.51 g, 82%, m.p.: 227-228 °C. IR, υ, cm^{-1}: 1513 (NCN). ^{1}H NMR ($CDCl_3$) δ, ppm: 1.01-1.22 (m, 4H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN); 1.57-1.73 (m, 4H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN); 3.17-3.31 (m, 2H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N); 1.32 and 1.34 (s, 18H, $CH_2C_6H_4C(CH_3)_3$-*p*); 5.08, 5.17, 5.31 and 5.44 (d, 4H, *J* = 4 Hz, C*H*$_2$Ar); 7.28 and 7.40 (d, 8H, *J* = 8 Hz, $CH_2C_6H_4C(CH_3)_3$-*p*); 1.16 and 1.20 (d, 6H, *J* = 8 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$); 2.04 (s, 3H, *p*-$CH_3C_6H_4CH(CH_3)_2$); 2.72 (sept, 1H, *J* = 8 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$); 4.64, 4.88, 5.58 and 5.80 (d, 4H, *J* = 16 Hz, *p*-$CH_3C_6H_4CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ, ppm: 23.1, 24.1, 29.2, 29.6, 53.9 and 55.0 (N*C*H(*C*H$_2$)$_4$*C*HN); 31.4 ($CH_2C_6H_4C(CH_3)_3$-*p*); 34.5 ($CH_2C_6H_4C(CH_3)_3$-*p*); 68.2 and 68.8 (*C*H$_2$Ar); 125.0, 125.9, 127.3, 135.0, 136.3 and 149.9 ($CH_2C_6H_4C(CH_3)_3$-*p*); 18.4 (*p*-$CH_3C_6H_4CH(CH_3)_2$); 21.8 (*p*-$CH_3C_6H_4CH(CH_3)_2$); 30.4 (*p*-$CH_3C_6H_4CH(CH_3)_2$); 83.3, 84.8, 85.8, 85.9, 96.9 and 107.5 (*p*-$CH_3C_6H_4CH(CH_3)_2$); 214.8 (Ru-C_{carb}).

2.5. General procedure for the *N*-alkylation of amines with alcohols

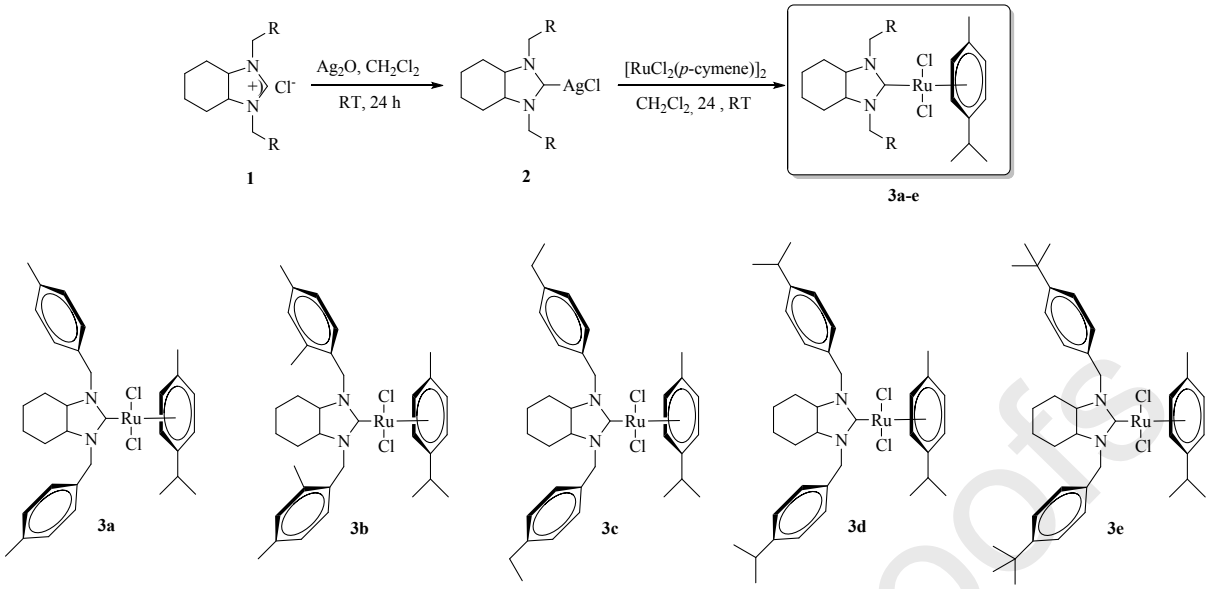
Under an inert atmosphere, KOBu^t (1 mmol), the aromatic amine (1 mmol), the alcohol derivative (1.5 mmol) and the Ru-NHC complex (2.5 mol%) were added to a Schlenk tube. The sealed Schlenk tube was stirred at 120 °C for 24 h. At the end of the reaction, the mixture was cooled to room temperature, CH_2Cl_2 (2 mL) was added and the resulting solution was filtered through a short pad of SiO_2. The filtrate was analysed by GC-MS with the calibrations based on dodecane.

3. Results and discussion

3.1. Synthesis of the Ru(II)-NHC complexes

The symmetrical 1,3-dialkylperhydrobenzimidazolium salts **1**, as NHC precursors, were obtained in high yields from the cyclization of the *N,N'*-dialkylcyclohexan-1,2-diamines with

triethyl orthoformate in the presence of ammonium chloride. The coordination of the perhydrobenzimidazol-2-yldene ligands to ruthenium was achieved by the transmetallation with silver *N*-heterocyclic carbene complexes. This procedure, involving Ag-NHC complexes, is probably one of the most general methods for the preparation of NHC complexes, which has successfully been applied to many transition metals, including ruthenium, rhodium, iridium, gold and nickel [35]. Treatment of the perhydrobenzimidazolium salts with Ag_2O in dichloromethane at room temperature in the dark afforded the corresponding silver NHC complexes **2**. The addition of $[RuCl_2(p\text{-cymene})]_2$ to a solution of the silver NHC complexes in dichloromethane gave the desired (*p*-cymene)-ruthenium(II)-NHC complexes **3a-e** in moderate to good yields (Scheme 1). Instant precipitation of AgCl indicated the successful carbene transfer onto ruthenium centre to form the ruthenium(II)-NHC complexes. The ruthenium(II)-NHC complexes were purified by crystallization. These complexes are very stable against air and moisture in the solid state. The new ruthenium complexes were characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy, together with elemental analysis techniques, which support the proposed structures. NMR analyses of the complexes showed that the *N*-heterocyclic carbene ligands had been transferred from the silver complexes to the ruthenium ion. They exhibit characteristic υ(C=N) bands in the range 1502-1517 cm^{-1} for **3a-e.** In the ^{1}H NMR spectra of **3a-e**, the benzylic protons signals of the *N*-heterocyclic carbene ligands appear as four doublets in range δ 4.99-5.44 ppm, with the same coupling constants, indicating that the methylene protons of the two benzyl groups are diastereotopic. The signals of non-equivalent aromatic protons of the *p*-cymene ligands were observed as four doublets in range δ 4.64-5.80 ppm in the ^{1}H NMR spectra of **3a-e**. The methyl signals of the isopropyl group on the *p*-cymene ligands appear as two doublets in range δ 1.09-1.24 ppm, whereas the methyl signals of the *p*-cymene ligands were observed as a singlet in range δ 1.86-2.06 ppm. The ^{13}C-NMR chemical shifts provide a useful diagnostic tool for this type of metal carbene complex. The resonance of the carbene carbon atom of complexes **3a-e** was observed at δ 214.8 ppm for **3a** and **3c-e**, and at δ 215.2 ppm for **3b**, these values are similar to those found for other (*p*-cymene)-ruthenium(II)-NHC complexes. These new complexes show typical spectroscopic signatures which are in line with those recently reported for other $[RuCl_2(NHC)(arene)]$ complexes [36,37].



Scheme 1. The synthesis of the (*p*-cymene)-ruthenium(II)-NHC complexes.

3.2. Crystal structure description of complex 3c

The molecular structure of complex **3c** was determined by the single-crystal X-ray diffraction technique and the obtained results confirmed all the spectroscopic data. A single crystal of complex **3c** for X-ray diffraction analysis was obtained by slow vapor diffusion of diethyl ether into a dichloromethane solution of **3c** at room temperature. The complex crystallized in the monoclinic C2 space group with $Z = 4$. Details of the crystallographic data and structure refinement parameters are summarized in Table 1. Since the low temperature apparatus of the Bruker APEX-II CCD diffractometer instrument was not in service, we collected single crystal X-ray diffraction data for complex **3c** at room temperature and we obtained some disorder problems in the molecular structure. However, it is clear that the obtained molecular structure for the complex **3c** confirms our suggested molecular structure. The atom numbering for complex **3c** is given in Figure 1 with the relevant bond distances and angles collected (see supporting information, Table S1).

Table 1. Crystal data and details of the structure refinement for complex **3c**.

Empirical formula	$C_{35}H_{44}Cl_2N_2Ru$
Formula weight	664.69
Temperature (K)	296.0(2)
Crystal system	Monoclinic
Space group	C2
a (Å)	49.015(3)
b (Å)	6.5288(3)
c (Å)	10.2986(5)
β (°)	96.749(2)
Volume (Å^3)	3272.8(3)
Z	4
ρ_{calc} (g/cm^3)	1.349
M (mm^{-1})	0.668
F(000)	1384.0
Crystal size (mm^3)	0.43 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection (°)	6.032 to 50.088
Index ranges	$-58 \leq h \leq 58$, $-7 \leq k \leq 7$, $-12 \leq l \leq 12$
Reflections collected	46193
Independent reflections	5793 [R_{int} = 0.0819, R_{sigma} = 0.0448]
Data/restraints/parameters	5793/1/367
Goodness-of-fit on F^2	1.078
Final R indexes [I≥2σ (I)]	R_1 = 0.0607, wR_2 = 0.1472
Final R indexes [all data]	R_1 = 0.0722, wR_2 = 0.1526
Largest diff. peak/hole (e Å^{-3})	1.93/-0.79
Flack parameter	0.082(17)

The ruthenium atom in the molecule has a classical pseudo-tetrahedral piano-stool coordination environment, being ligated by two chloride ligands, one carbon atom of the *N*-heterocyclic carbene ligand and a η^6-*p*-cymene ligand.

The Ru-C_{carben} [2.072(11) Å] and the average Ru-C_{cymene} [2.207(12) Å] and the average Ru-Cl [2.427(3) Å] bond lengths are slightly elongated in comparison with those observed previously in related ruthenium complexes [38-41]. The Ru-Cl distances in the coordination sphere are equal to within experimental error [Ru-Cl1 = 2.427(3) Å and Ru-Cl2 = 2.428(4) Å]. The ruthenium atom is situated 1.708(5) Å from the ring centroid of the η^6-*p*-cymene ligand and the angles of the ring centroid of the *p*-cymene ligand–Ru–Cl are 127.1(2) and 127.4(2)° [38]. The bond angles Cl1-Ru-Cl2 [83.70(14)°] and Cl-Ru-C_{carben} [89.8(3) and 89.0(3)°] fall within the normal range for known analogous complexes [39-42]. The small steric demand of the carbene ligand is reflected in the 89.8(3) and 89.0(3)° C–Ru–C1 angles. All the other bond lengths and angles fall within the expected range. A part of the benzimidazole ring (C2-C3-C4-C5-C6) exhibits a puckered conformation, with puckering

parameters q_2 = 0.161(16) Å, q_3 = 0.581(16) Å, Q_T = 0.604(15) Å, θ = 15.6(15)° and φ = 316(6)° [43]. The largest deviations from the mean plane are 0.327(12) Å for C7 and 0.304(14) Å for C2. This ring puckering analysis shows that the C2-C7 ring has a chair conformation with equatorial substitution at C2 for N1.

In the crystal structure, the molecules are linked by an intermolecular short contact: C26-H26···Cl1^{i}, with C-H 0.93 Å, H···Cl 2.64 Å, C-H···Cl 169° [Symmetry code: (i) x, -1+y, z] and an intramolecular short contact: C17-H17B···Cl1, C-H 0.97 Å, H···Cl 2.55 Å, C-H···Cl 129°.

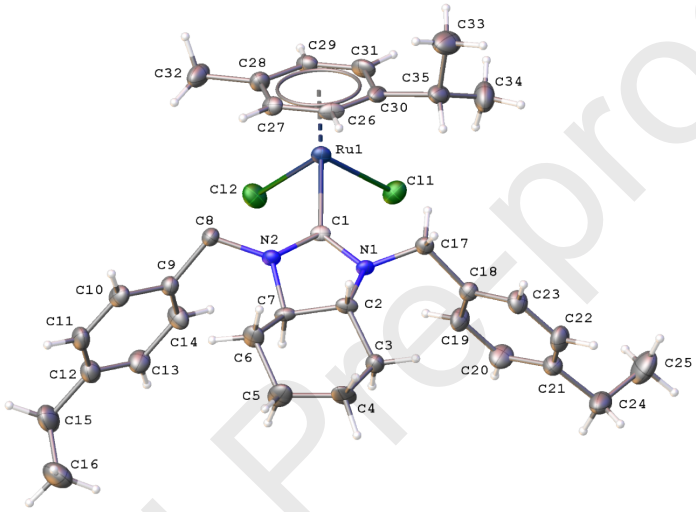


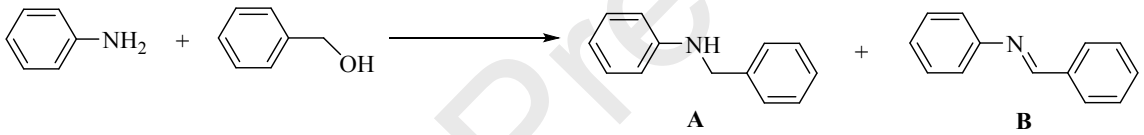
Figure 1. Molecular structure of the complex **3c**.

3.3. Catalytic studies

The catalytic activities of the new ruthenium complexes **3a-e** for the *N*-alkylation of aromatic amines with arylmethyl alcohols were evaluated. Initially, the reaction of aniline with benzyl alcohol was selected as a model reaction to determine the optimal catalytic conditions, with **3e** as a catalyst. The effect of the base, reaction time, solvent and catalyst loading were examined. The results are summarized in Table 2. A base was crucial to the efficiency of these reactions. Cs_2CO_3, K_2CO_3, KOH, and KOBu^{t} were tested as the base. Among the tested bases, KOBu^{t} displayed the highest reactivity (entry 3). KOH was less effective (entry 2), while the alkali metal carbonates Cs_2CO_3 and K_2CO_3 stopped the reaction completely at the dehydrogenation step. It is noteworthy that in the absence of a base or ruthenium complex, no reaction was observed (entry 11). Toluene and dioxan, often used in these reactions, gave excellent or poor conversions (entries 2 and 5). However, in the absence of a solvent, an excellent conversion was also observed. Reducing the catalyst loading to 1

mol% decreased the conversion (entry 9). Excellent conversion and selectivity were obtained the use of 2.5 mol% of **3e** (entry 10). A lower temperature (100 °C) or shorter time (15 h) reduced the conversion (entries 2 and 1), whereas full conversion was observed at 120 °C for 24 h (entry 7). The catalytic experiments were carried out using 1 mmol aromatic amine, 1.5 mmol arylmethyl alcohol, 1.0 mmol KOBu^t, and 0.025 mmol **3a-e** at 120 °C for 24 h under argon without any solvent or additive. Under these reaction conditions, the ruthenium catalyzed *N*-alkylation of aromatic amines (aniline, 2,4-dimethylaniline, and 2-aminopyridine) with arylmethyl alcohols (benzyl alcohol, 4-methyl benzyl alcohol, 4-methoxybenzyl alcohol and furfuryl alcohol) were examined. In all cases, only mono-alkylated amines and imines were formed; no bis-alkylated products were detected. The reaction products were characterized by NMR spectroscopy. The conversions and selectivities were screened by GC and GC-MS analysis.

Table.2. Determination of reaction conditions for the alkylation of aniline with benzyl alcohol.[a-h]



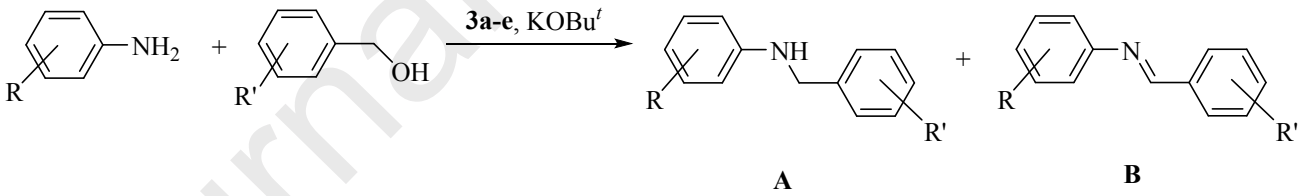
A **B**

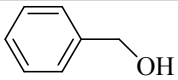
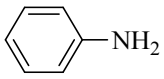
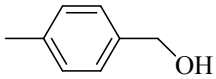
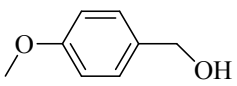
Entry	3e (mol%)	Base	Time (h)	Temp (°C)	Conversion (%)	A/B (%)
1	1	KOH	15	100	50	36/64
2	1	KOH	24	100	73	44/56
3	1	KOBu^t	24	100	83	57/43
4	1	KOH	24	150	88	49/52
5	1	KOH	24	100	9	13/87[b]
6	1	KOBu^t	24	120	90	78/22
7	2.5	KOBu^t	24	120	100	89/11
8	2.5	KOBu^t	24	120	97	52/48[c]
9	1	KOBu^t	24	120	84	60/40[d]
10	2.5	KOBu^t	24	120	100	88/12[d]
11	-	-	24	120	no reaction	-/-

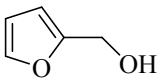
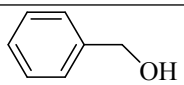
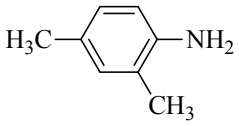
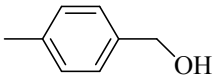
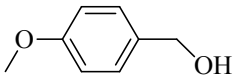
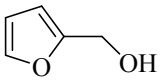
[a]Reaction conditions: Aniline (1 mmol), benzylalcohol (1.5 mmol), base (1 mmol), Ru-NHC (0.01 mmol), toluene (3 mL), 15-24 h, 100 °C. [b]Dioxane. [c]Base (0.5 mmol). [d]Solvent free. Yields are determined by GC and GC-MS.

With the determined optimal conditions in hand, we first investigated, in the presence of complexes **3a-e** as catalysts, the *N*-alkylation of aniline with benzyl alcohol, 4-methylbenzyl alcohol, 4-methoxybenzyl alcohol and furfuryl alcohol. In all the reactions, alkylation of aniline with high selectivities was achieved. The reaction of aniline with benzyl alcohol gave *N*-benzylaniline with 93-100% conversions (Table 3, entry 1). The formation of *N*-benzylaniline with high selectivity was obtained with complex **3d** (Table 3, entry 1). The treatment of aniline with 4-methylbenzyl alcohol and 4-methoxybenzyl alcohol using complexes **3a-e** as catalysts also gave the corresponding mono-alkylated amines, with conversions of 96-99% and 86-94%, respectively, under these conditions. 4-Methoxybenzyl alcohol afforded the corresponding mono-alkylated product *N*-(4-methoxybenzyl)aniline with excellent selectivities for all the complexes **3a-e** (Table 3, entry 3). The best selectivity was achieved with catalyst **3e** (Table 3, entry 3). These results show that the electron-donating substituent (4-methyl and 4-methoxy) on the benzyl alcohol gave higher selectivity when compared benzyl alcohol itself. When using furfuryl alcohol as an alkylating agent, *N*-(furan-2-ylmethyl)aniline with 100% selectivity was obtained for all the complexes **3a-e**, but the conversions of reactions were slightly lower than the other alkylating agents (Table 3, entry 4).

Table 3. *N*-alkylation of anilines with benzyl alcohols.[a]



Entry	Amine	Alcohol	[Ru] Conversion (Yield A:B%)				
			3a	**3b**	**3c**	**3d**	**3e**
1			95 (80/20)	98(70/30)	95(57/43)	93(98/2)	100(88/12)
2			96(100/0)	98(86/14)	96(70/30)	99(80/20)	97(100/0)
3			90(99/1)	94(97/3)	86(98/2)	86(99/1)	93(100/0)

4			94(100/0)	88(100/0)	87(100/0)	83(100/0)	85(66/34)
5			73(81/19)	69(51/49)	78(57/43)	81(94/6)	71(94/6)
6			86(89/11)	95(82/18)	88(100/0)	98(100/0)	84(50/50)
7			82(54/46)	81(80/20)	86(65/35)	100(97/3)	83(76/24)
8			84(100/0)	81(100/0)	85(100/0)	92(100/0)	79(66/34)

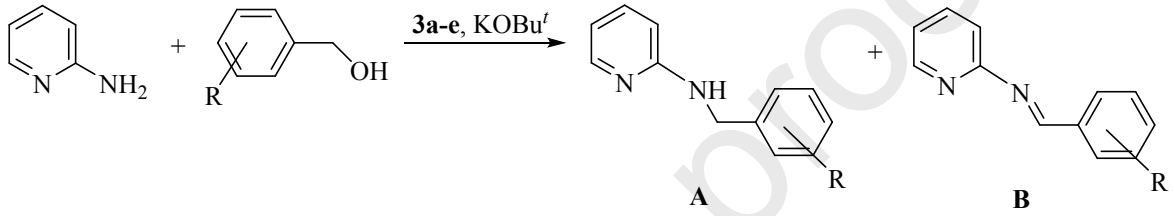
[a]Reaction conditions: Complexes **3a-e (**0.025 mmol), arylmethyl alcohol (1.5 mmol), heterocyclic amine (1 mmol), KOBu^t (1 mmol), 120 °C, 24 h. The conversions and the selectivities were determined by GC and GC-MS analysis with calibrations based on dodecane.

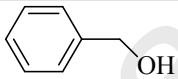
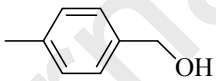
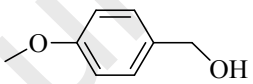
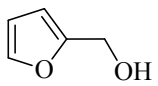
We next examined the reactions of 2,4-dimethylaniline with benzyl alcohol, 4-methylbenzyl alcohol, 4-methoxybenzyl alcohol and furfuryl alcohol in the presence of complexes **3a-e** as catalysts under the same reaction conditions (Table 3, entries 5-8). Thus, 2,4-dimethylaniline was treated with benzyl alcohol for all the complexes **3a-e** under the optimized reaction conditions to obtain the corresponding *N*-benzyl-2,4-dimethylaniline in 69-81% conversions with 51-94% selectivities (Table 3, entry 5). The reaction of 2,4-dimethylaniline with 4-methylbenzyl alcohol and 4-methoxybenzyl alcohol also afforded the corresponding mono-alkylated amines with conversions of 84-95% and 81-100%, with 50-100% and 54-97% selectivities, respectively. The above results show that electron-donating substituents, such as Me and Ome, on both benzyl alcohol and aniline slightly increased the selectivities of the mono-alkylated amine products under the same conditions (Table 3, entries 1-3 and Table 3, entries 5-7). Similar trends have been observed for the other Ru(II) systems bearing NHC ligands [22]. When furfuryl alcohol was used as an alkylating agent, only the corresponding mono-alkylated amine was obtained, with 100% selectivity for complexes **3a-d** (Table 3, entry 8); only **3e** gave a slightly lower result than the other complexes. No imine or bis-alkylated products were detected.

Finally, we also investigated the *N*-alkylation of 2-aminopyridine with the same alcohols (benzyl alcohol, 4-methylbenzyl alcohol, 4-methoxybenzyl alcohol and furfuryl alcohol), using the ruthenium(II)-NHC catalysts **3a-e** in order to obtain *N*-alkylated amines under the same reaction conditions. The 2-(*N*-alkylamino)pyridines were obtained in good to excellent selectivities in the presence of 2.5 mol% of the catalysts. Moreover, the heteroaromatic

moiety in 2-aminopyridine was also well-tolerated under this catalytic system. In all the reactions, only the nitrogen atom of the amino group of 2-aminopyridine was alkylated, the products with *N*-alkyl pyridine were not detected. 2-Aminopyridine was efficiently arylated with benzyl alcohol and furfuryl alcohol for all the complexes **3a-e** with 100% selectivity (Table 4, entries 1 and 4). The reaction of 2-aminopyridine with 4-methylbenzyl alcohol and 4-methoxybenzyl alcohol also gave the corresponding products with conversions of 96-100% and 98-100%, with 99-100% and 97-100% selectivities, respectively.

Table 4. *N*-alkylation of 2-pyridyl amine with arylmethyl alcohols.[a]

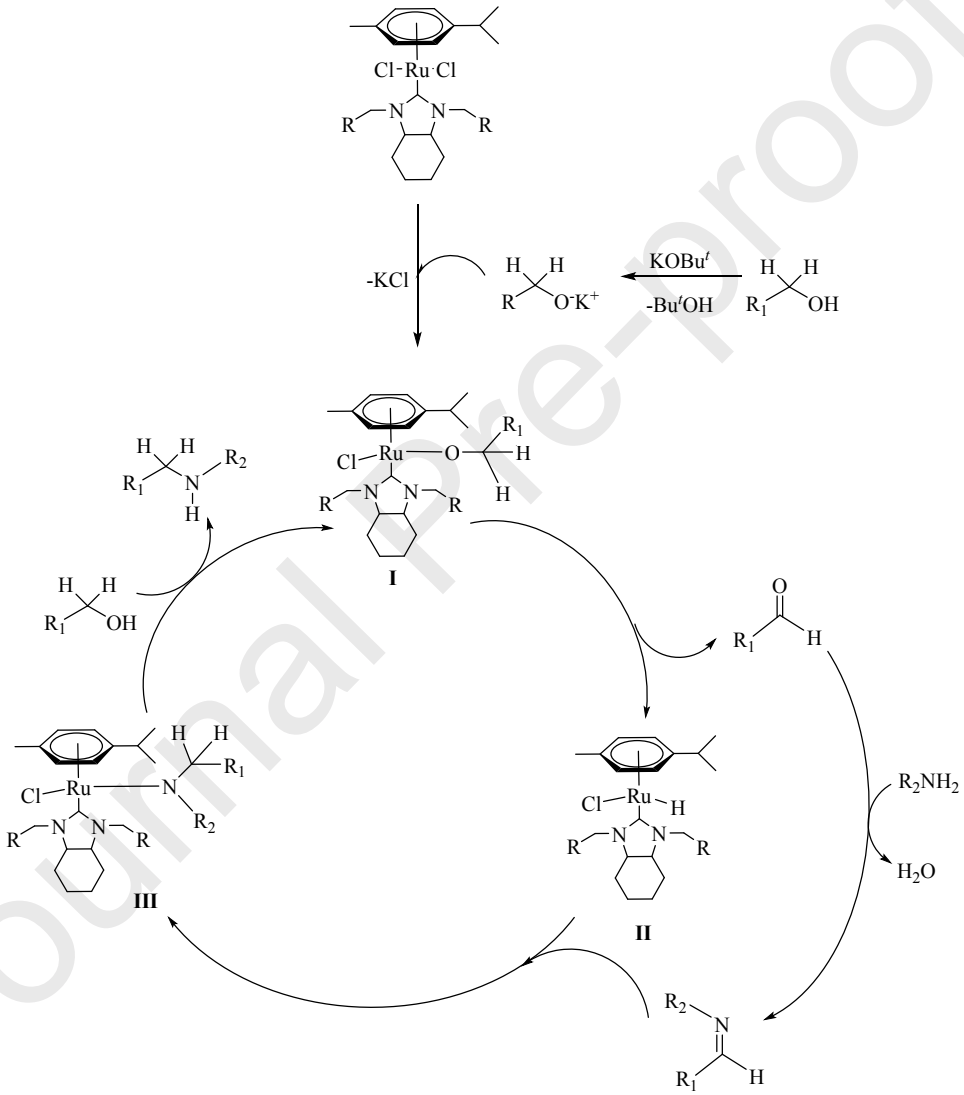


Entry	Alcohol	[Ru] Conversion (Yield A:B%)				
		3a	**3b**	**3c**	**3d**	**3e**
1		98(100/0)	98(100/0)	97(100/0)	96(100/0)	98(100/0)
2		100(100/0)	97(100/0)	96(100/0)	98(100/0)	99(99/1)
3		99(98/2)	100(98/2)	100(97/3)	100(97/3)	98(97/3)
4		95(100/0)	92(100/0)	97(100/0)	95(100/0)	100(100/0)

[a]Reaction Conditions: Aniline (1 mmol), alcohol (1.5 mmol), Ru-NHC (0.025 mmol), KOBu^t (1 mmol), 120 °C, 24 h. The conversions and the selectivities were determined by GC and GC-MS analysis with calibrations based on dodecane.

The ruthenium(II)-NHC complexes showed good catalytic activity for the N-alkylation of amines in the presence of KOH base, and the general mechanism reveals that the in situ generated ruthenium hydride species is the catalytically active species [44, 45]. A possible catalytic cycle is proposed in Scheme 2 on the basis of the results obtained and available

literature on similar ruthenium catalyzed transformations [46-48]. This catalysis is considered to proceed via the (benzyloxy)ruthenium intermediate **I**, which undergoes β-hydrogen elimination to give the ruthenium hydride **II**. Dehydrative condensation of the aldeyde with an amine forms an imine ($R_1CH{=}NR_2$). Insertion of the imine into the Ru-H bond of **II**, followed by alcoholysis of the resulting (amido)ruthenium species **III**, affords the N-alkylation product and reproduces the (benzyloxy)ruthenium intermediate **I**, completing the catalytic cycle.



Scheme 2. A proposed reaction pathway for the ruthenium(II)-NHC catalyzed N-alkylation.

4. Conclusion

In summary, ruthenium(II)-NHC complexes **3a-e** have been easily prepared by the reaction of silver(I)-NHC complexes as a carbene transfer reagent with $[RuCl_2(p\text{-cymene})]_2$ in

dichloromethane at room temperature in good yields and the molecular structure of compound **3c** has also been determined by X-ray crystallography. The catalytic activity of these complexes was investigated for the *N*-alkylation reactions of aniline, 2,4-dimethylaniline and 2-aminopyridine with arylmethyl alcohols, including benzyl alcohol, 4-methyl benzyl alcohol, 4-methoxybenzyl alcohol and furfuryl alcohol. The *N*-alkylation of the amines was performed under solvent-free conditions over 24 h at 120 °C using 2.5 mol% of complexes **3a-e**. All of these complexes were found to be suitable for the *N*-alkylation of aromatic amines with arylmethyl alcohols via hydrogen borrowing reactions. In this study, high selectivities were obtained. In all cases only monoalkylated amines were formed and no bis-alkylated products were detected.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Appendix A. Supplementary data

CCDC 1910177 contains the supplementary crystallographic data for **3c**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Active ruthenium(II)-NHC complexes for alkylation of amines with alcohols using solvent-free conditions

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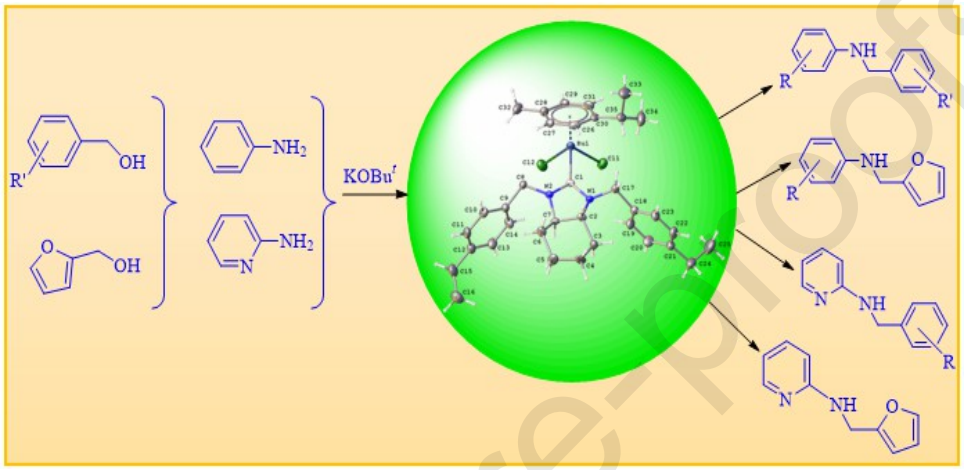

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A series of new ruthenium(II) complexes bearing *N*-heterocyclic carbene ligands with benzylic groups were prepared by transmetallation reactions between silver(I) *N*-heterocyclic carbene complexes and $[RuCl_2(p\text{-cymene})]_2$. All of the obtained complexes were characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy, and the molecular structure of compound **3c** was also determined by X-ray crystallography. These ruthenium complexes were tested for the alkylation of aromatic amines with a wide range of primary alcohols under solvent-free conditions using the hydrogen borrowing strategy. All of the compounds tested

here showed excellent catalytic activity for these reactions and *N*-monoalkylated products were obtained selectively using 2.5 mol % of the ruthenium complexes.