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Synthesis of ruthenium N-heterocyclic carbene complexes and their catalytic activity for β-alkylation of tertiary cyclic amines

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ABSTRACT

The novel ruthenium *N*-Heterocyclic carbene complexes are synthesized, and characterized by studying its ^{1}H, ^{13}C, elemental analysis, and X-ray. These complexes have been reported as promising catalyst for β C–H bond functionalization of tertiary cyclic amines through hydrogen autotransfers in the presence of external acidic additive. The new catalytic products were characterized by ^{1}H NMR, ^{13}C NMR spectroscopic methods.

1. Introduction

Considering the importance of selective deuteration [1], racemisation [2] and functionalization [3], to access valuable azaheterocycles, oxidant free hydrogen transfer processes enabling either α and/or β C–H bonds activation/functionalization adjacent to nitrogen atom have attracted lot of interest. Selective redox neutral alkyl exchanges [4] or dehydrogenative hydrolyzes [5] of amines in the presence of catalytic amount of palladium black were reported by Murahashi and coworkers. Later on, Shvo and Laine demonstrated that homogeneous $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ were efficient precatalysts for similar alkyl exchanges [6]. The ruthenium catalysts are well-known for hydrogen transfer from alcohols, they have not been used for dehydrogenation of cyclic amines except for alkylation of anilines. We have thus investigated the possibility of performing a sequence of catalytic reactions from cyclic amines with ruthenium catalysts based on hydrogen transfers according to Fig. 1.

Since then, other groups extended these concepts to enable the α-alkylation of amines in the presence of platinum(II) [7] whereas alkynylation, α,β deuteration were successfully achieved in the presence of Shvo's complex [8]. Replacing tertiary amine by secondary amine in the presence of a Ru(PNP) precatalyst and water enable the formation of amides [9]. The transient formation of enamine intermediates in the presence of ruthenium or iridium complexes allowed the access to β-alkylated products with aldehydes acting as electrophiles [10]. To date, β-alkylation of saturated tertiary amines involving hydrogen autotransfers have been reported with ruthenium complexes embedded with a phosphine-sulfonate chelate whereas nothing is known about the use of NHC ligands or external acidic additive in related transformations.

Since the discovery of stable free N-heterocyclic carbene (NHC) [11], metal carbene complexes based on imidazol-2-ylidene (imy) or benzimidazol-2-ylidene (bimy) have received considerable attention both in organometallic chemistry and homogeneous catalysis [12]. As regards ruthenium, most of the known NHC-catalysts have been applied to olefin metathesis [13], C–C alkyne coupling [14] and hydrogenation [15] reactions. N-Heterocyclic carbenes are generally derived from imidazoles [16–20], benzimidazoles [21–24], triazoles [25–28] and pyrazoles [29–33]. Functionalization on nitrogen atoms enlarge the scope of these proligands. Owing to these aforementioned tuneable steric and electronic properties, catalytic activities of the resulted NHC complexes are greatly affected. Our group has prepared a series of ruthenium-NHC complexes bearing chelating imidazoline or benzimidazole, bidentate imidazoline-based carbene ligands and tested their catalytic activities in the metathesis and C–H bond

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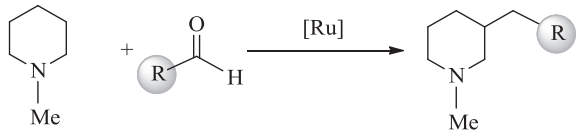


Fig. 1. Functionalization of cyclic amine involving hydrogen transfer processes.

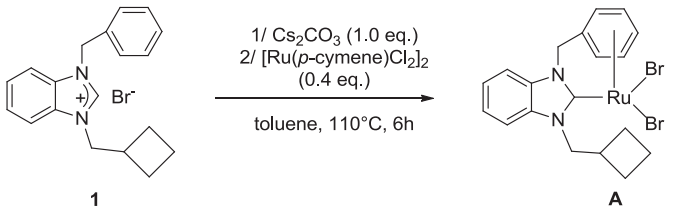
activation reactions [34].

In this paper, we report the synthesis and characterization of a series of new ruthenium(II) complexes with carbene ligands bearing hemilabile arene side arm. The influence of the acidic additive is evaluated during the non-destructive β-alkylation of *N*-methylpiperidine with various aldehydes as electrophile.

2. Results and discussion

2.1. Synthesis of ruthenium NHC complexes

In this context, the easily accessible and stable Ru dimer [(*p*-cymene)$RuCl_2$]$_2$ is an easy metallic precursor to handle that is an ideal starting material for the synthesis of benzimidazolin-2-ylidene ruthenium catalysts to be further used for alkylation of cyclic amines. Many synthetic methods for the synthesis of metal-NHC complexes have been explored. According to these reports, the most widely used preparation methods can be divided broadly into five types: (i) reaction of *in situ* generated free NHCs with metal precursors [35], (ii) reaction of electron-rich olefin dimers with organometallic fragments [36], (iii) reaction of imidazolium salts with suitable basic transition metal salts [37], (iv) reaction of azolium salts with metal precursors under basic phase transfer catalysis (PTC) conditions [38], and (v) transmetallation with Ag(I)–NHCs [39]. Additionally, Delaude has shown that imidazol(in)ium-2-carboxylates readily lost their CO_2 moiety upon heating or dissolution and could serve as efficient carbene precursors in organocatalytic processes or for the synthesis of various transition metal-NHC complexes [40]. We evaluated two pathways for the synthesis of our ruthenium NHC complexes. The first method **I** (Scheme 1) involved reaction of electron-rich olefin dimers with organometallic fragments under refluxing toluene allowing the formation of the chelating complex **A**. NMR analysis confirmed the loss of the *p*-cymene ligand. Selective crystallization by solvent diffusion technique (CH_2Cl_2/hexane) allowed the formation of suitable orange-brown crystals for X-ray diffraction analysis. Fig. 2 displays the molecular structure of complex **A**. The ruthenium complex displays half sandwich structure where the aromatic moiety of the benzylic arm play the role of η^6-arene ligand. Noteworthy that selective halogen exchange occurred between the chloride ligand of the starting metal precursor and the bromide counteranion of the benzimidazolium bromide. In contrast, under milder reaction conditions, by using transmetallation methodology **II** with Ag(I)–NHCs arising from **2** and **3** and the corresponding metal precursor [Ru(*p*-cymene)Cl_2]$_2$ prevented the removal of the *p*-cymene ligand affording the corresponding [$RuCl_2$(arene)NHC] (arene = *p*-cymene) complexes **B** and **C**. (Scheme 2).



Scheme 1. Preparation of complex **A**.

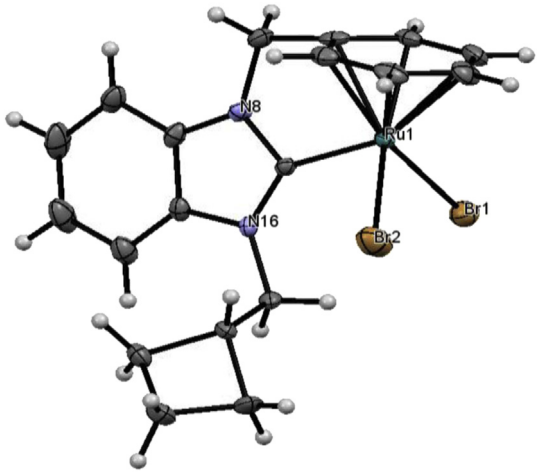
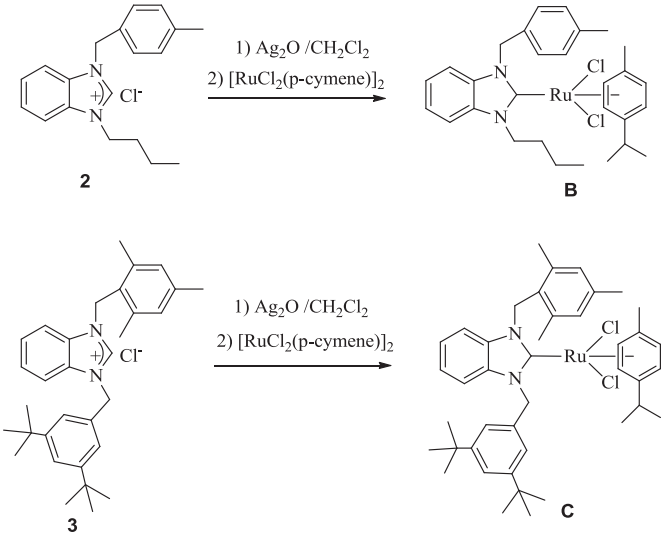


Fig. 2. Molecular structure of complex **A**. Selected bond lengths [Å] and angles [°]: Ru-(1)-Br(1) 2.540(1), Ru(1)-Br(2) 2.5028(8), Ru(1)-C(9) 2.045(6); Br(2)-Ru(1)-Br(1) 90.9°; Br(2)-Ru(1)-C(19) 94.0°.

2.2. Application in β-alkylation

With these well-defined complexes in hand, we next undertook their preliminary evaluation in oxidant free C–H bond functionalization of tertiary cyclic amines in the presence of electrophile to rationalized the effect of the hemilabile shielding character of the side arm of the benzylic moiety toward activity and selectivity. On the other hand, *N*-methylated amines represent an interesting class of biologically active compounds and selective functionalization keeping intact the methyl group is attractive. However, during β-alkylation, the competitive formation of *exo* and *endo*-cyclic iminium would result in undesired demethylation reaction through the attack of nucleophile on the resulting *exo*-cyclic iminium. A plausible mechanism is depicted for give point to the role of CSA in Chart 1.

For this purpose we decided to evaluate the challenging *N*-methyl piperidine material which can easily undergo hydrolysis of the methyl group under hydrogen autotransfer conditions. The screening of our new ruthenium complexes **A-C** was performed in toluene with benzaldehyde, in the presence of substoichiometric



Scheme 2. Preparation of complex **B** and **C**.

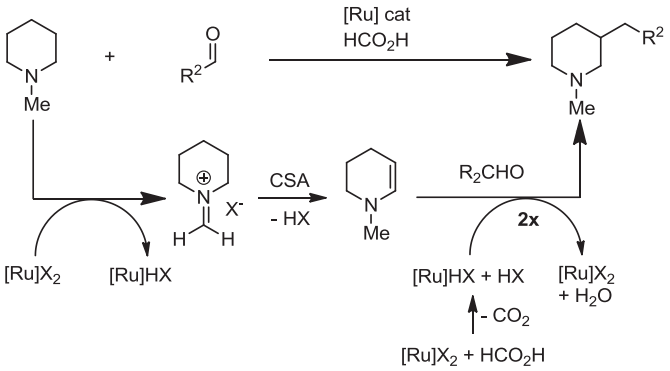


Chart 1. Proposed mechanism.

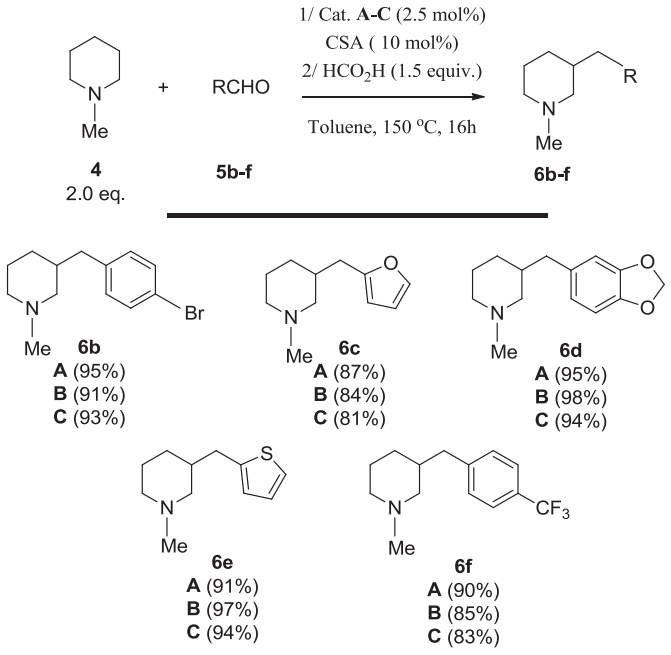


Chart 2. Scope of the β-alkylation of *N*-methylpiperidine **4**.

amount of complex **A**-**C** (2.5 mol%). The addition of formic acid at the end of the reaction ensure complete conversion of the β-alkylated enamine to the corresponding amines (Table 1).

Firstly, we examined the reactivity of precatalyst **A** in the presence of a slight excess of *N*-methylpiperidine **4** (1.1 eq.) along with 10 mol% of camphor sulfonic acid (CSA). In this case, formation of the expected β-alkylated product **6a** occured but side formation of the disusbstituted β-alkylated product reached a 58:42 ratio of **6a**:**7** (entry 1). Importantly, this result contrasted with the previously reported ruthenium complexes containing phosphinesulfonate chelates which favored the mono alkylation under stoichiometric reaction conditions. Gratifyingly, the *N*-methyl substituent remained intact and only few traces of demethylated side product were observed.

To overcome the undesired formation of the dialkylated product **7** we next examined the influence of the CSA amount. Thus, lowering the catalytic loading of CSA to 5 mol% diminished side dialkylation reaching complete conversion and 87:13 ratio of **6a**:**7** (entry 3). Another strategy to reduce side dialkylation involved the use of a large excess of piperidine (2.0 eq.) to give a ratio up to 83:17 (entry 2). The influence of the ruthenium complex was next investigated. Notably, complete conversions were obtained in the presence of catalytic amount of complex **B** and **C** and the best ratio was observed in the presence of complex **C** bearing two sterically hindered benzylic side arms (entries 4 compared to 5).

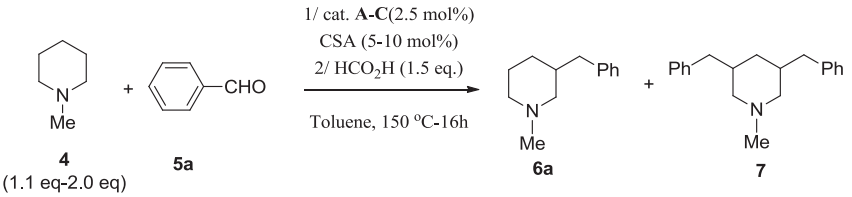
We our best reaction conditions in hands, we next evaluated the scope of the transformation with various aldehydes (Chart 2).

The reaction appeared to be quite general and good results were obtained from the reaction of **4** with *p*-bromobenzaldehyde yielding up to 95% of product **6b**. Heteroaromatic aldehydes such as 2-furfural and 2-thiophene carboxaldehyde were compatible and yields up to 87 and 97% were obtained for **6c** and **6e**, respectively. The acetal moiety in piperonal **5d** is quite sensitive functional group under hydrogen autotransfer conditions. Nevertheless, the use of precatalyst **B** bearing both an aliphatic side chain and a benzylic hemilabile side arm gave almost complete conversion to the expected compound **6d**.

3. Conclusions

In summary, we reported new NHC based ruthenium(II) complexes bearing hemilabile arene side arm. Altogether these results demonstrated the first application and the potential ruthenium bearing NHC ligand in sp^3 C–H functionalization of cyclic amines to access various β-alkylated *N*-methylpiperidine derivatives from easily available aldehydes and amines generating water as the only side product. This report highlighted the crucial influence on the acidic additive towards the generation of *endo* cyclic iminium. Our

Table 1
Ruthenium NHC catalyzed alkylation of *N*-methyl piperidine.



Entry[a]	Cat.	Amount of CSA/amount of amine	Ratio **6a**/7	Conv.[b]
1	**A**	10 mol%/1.1 eq.	58/42	78%
2	**A**	10 mol%/2.0 eq.	83/17	100%
3[c]	**A**	5 mol%/1.3 eq.	87/13	100%
4	**B**	10 mol%/2.0 eq.	79/21	100%
5	**C**	10 mol%/2.0 eq.	89/11	100%

[a] All reactions were carried out under an inert atmosphere.
[b] Conversion determined by GC analyses.
[c] 24 h.

current effort is to examine the activity of NHC bearing acidic side arm in similar transformations.

4. Experimental section

4.1. Materials and methods

All reactions performed to prepare the benzimidazolium salts and metal complexes were carried out under argon in flame-dried glassware using standard Schlenk techniques. Glassware was heat-dried in vacuum. Chemicals and solvents were purchased from Sigma–Aldrich (Gillingham,UK). Benzimidazolium salts as NHC precursors were synthesized according to our previous literature [41]. Solvents were dried with standard methods and freshly distilled prior to use. Elemental analyses were carried out by TUBITAK analytical services with a Carlo Erba (Milan, Italy) Strumentaziona model 1106 apparatus, and the results agreed favorably with the calculated values. Melting points were measured in open capillary tubes with a Thermo Scientific (Waltham, MA, USA) Electrothermal 9200 melting point apparatus. FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on an ATI Unicam (Cambridge, UK) 1000 spectrometer. MS analyses were performed on an Agilent Technologies (Santa Clara, CA, USA) 1100 series LC/MSD SL mass spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded using a Varian (Palo Alto, CA, USA) As 400 Merkur spectrometer operating at 400 MHz (^1H) and 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane used 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 d downfield from tetramethylsilane (d = 0.00), used 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. All catalytic reactions were monitored on a Agilent 6890N GC system by GC-FID with a HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Column chromatography was performed using silica gel 60 (70–230 mesh). The structure was solved by direct methods using the *SIR97* program [42], and then refined with full-matrix least-square methods based on F^2(*SHELXL-97*) [43] with the aid of the *WINGX* [44] program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 4158 unique intensities and 205 parameters converged at $\omega R(F^2) = 0.1527$ ($R(F) = 0.0511$) for 3525 observed reflections with $I > 2\sigma(I)$. (C_{19} H_{20} Br_2 N_2 Ru); M = 537.26. APEXII, Bruker-AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 150(2) K; monoclinic P $2_1/n$(I.T.#14), a = 10.5527(6), b = 10.9516(5), c = 16.2288(8) Å, β = 104.520(2)°, V = 1815.64(16) $Å^3$.Z = 4, d = 1.965 g cm^{-3}, μ = 5.268 mm^{-1}.

4.2. Synthesis and characterization of ruthenium N-heterocyclic carbene complexes

4.2.1. Dibromo-[1-(η^6–benzyl)-3-cyclobutylmethyl]benzimidazol-2-ylidene]ruthenium(II), ***A***

A suspension of benzimidazolium salt (2.10 mmol), Cs_2CO_3 (2.14 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (0.82 mmol) was heated under reflux in degassed toluene (20 mL) for 6 h. The reaction mixture was then filtered while hot, and the volume was reduced to about 10 mL before addition of n-hexane (15 mL). The precipitate formed was crystallized from CH_2Cl_2/hexane (5:15 mL) to give of orange-brown crystals.

^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.78–1.67 (m, 2H, CH_2, CH_2-*cyclobutane*); 2.23–2.01 (m, 4H, CH_2, CH_2-*cyclobutane*); 3.42 (hept., 1H, J = 8.1 Hz, C*H*, CH_2-*cyclobutane*); 4.82 (d, 2H, J = 7.8 Hz, CH_2-cyclobutane); 5.97 (s, 2H, $CH_2C_6H_5$); 7.10–7.82 (m, 9H, $CH_2C_6H_5$ and C_6H_4). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 18.4 (*C*H_2, CH_2-*cyclobutane*); 26.9 (*C*H_2, CH_2-*cyclobutane*); 36.1 (*C*H, CH_2-*cyclobutane*); 53.6 (*C*H_2-cyclobutane); 53.1 (*C*$H_2C_6H_5$); 134.7, 132.9, 125.8, 123.2, 113.8 and 111.2 (*C*$_6H_4$); 100.3, 99.1, 98.9, 98.7, 89.3 and 88.7 ($CH_2C_6H_5$); 180.3 (Ru-carbene); m.p.= 275–276 °C, $\nu_{(CN)}$ = 1408 cm^{-1}, yield 53%. Anal. Calcd for $C_{19}H_{20}N_2RuBr_2$: C: 42.48; H: 3.75; N: 5.21. Found C: 42.45; H: 3.70; N: 5.19%.

4.2.2. Dichloro [1-(n-butyl)-3-(4-methylbenzyl)benzimidazol-2-ylidene] (p-cymene) ruthenium(II), ***B***

Silver oxide (1.0 mmol) was added to a solution of benzimidazolium salt (2.0 mmol), in dichloromethane (30 mL), solution was stirred for 12 h under dark condition. The resulting solution was filtered, then $RuCl_2$(*p*-cymene)]$_2$ (0.5 mmol) was added to above solution. The solution was stirred for 12 h. The resulting solution was filtered and concentrated to 10 mL, and Et_2O (20 mL) was added and product was obtained as a crystallize solid.

^1H NMR (300 MHz, $CDCl_3$): δ 1.04 (t, J = 7.0 Hz, 3H, $NCH_2CH_2CH_2CH_3$); 1.25 (h, J = 7.0 Hz, 2H $NCH_2CH_2CH_2CH_3$); 1.30 (d, J = 6.9 Hz, 6H, *p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 2.01 (s, 3H, *p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 2.34 (s, 3H, $NCH_2C_6H_4(CH_3)$-4); 2.89 (m, 1H, *p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 2.98 (p, J = 7.0 Hz, 2H, $NCH_2CH_2CH_2CH_3$); 4.39 (t, J = 7.3 Hz, 2H, $NCH_2CH_2CH_2CH_3$); 5.36 (d, J = 7.5 Hz, 2H, *p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 5.45 (s, 2H, $NCH_2C_6H_4(CH_3)$-4); 5.32–5.70 (m, 2H, *p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 6.95–7.50 (m, 8H, NC_6H_4N and $NCH_2C_6H_4(CH_3)$-4). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9 ($NCH_2CH_2CH_2CH_3$); 18.6 ($NCH_2CH_2CH_2CH_3$); 20.4 (*p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 21.1 (*p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 30.6 (*p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 32.3 ($NCH_2C_6H_4(CH_3)$-4); 32.4 ($NCH_2CH_2CH_2CH_3$); 50.2 ($NCH_2CH_2CH_2CH_3$); 52.3 ($NCH_2C_6H_4(CH_3)$-4); 83.6, 87.2, 98.9, and 108.5 (*p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 110.8, 111.6, 122.8, 122.9, 125.8, 129.5, 134.6, 135.1, 135.8, 137.1, (NC_6H_4N and $NCH_2C_6H_4(CH_3)$-4); 189.6 (Ru-carbene); m.p.= 213–214 °C, $\nu_{(CN)}$ = 1438 cm^{-1}, yield 85%. Anal. Calcd for $C_{29}H_{36}N_2RuCl_2$: C: 59.58; H: 6.21; N: 4.79. Found C: 59.52; H: 6.25; N: 4.73%.

4.2.3. Dichloro[1-(2,4,6-trimethylbenzyl)-3-(3,5-di-ter-butylbenzyl)benzimidazol-2-ylidene] (p-cymene) ruthenium(II), ***C***

Silver oxide (1.0 mmol) was added to a solution of benzimidazolium salt (2.0 mmol), in dichloromethane (30 mL), solution was stirred for 12 h under dark condition. The resulting solution was filtered, then $RuCl_2$(*p*-cymene)]$_2$ (0.5 mmol) was added to above solution. The solution was stirred for 12 h. The resulting solution was filtered and concentrated to 10 mL, and Et_2O (20 mL) was added and product was obtained as a crystallize solid.

^1H NMR (300 MHz, $CDCl_3$): δ 1.27 (s, 18H, $NCH_2C_6H_3(C(CH_3)_3)$-3,5); 1.32 (d, J = 6.9 Hz, 6H, *p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 2.19 and 2.31 (s, 9H, $NCH_2C_6H_2(CH_3)_3$-2,4,6); 2.07 (s, 3H, *p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 2.82 (hept. J = 6.9 Hz, 1H, *p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 5.30 (s, 2H, $NCH_2C_6H_2(CH_3)_3$-2,4,6); 5.32 (s, 2H, $NCH_2C_6H_3(C(CH_3)_3)$-3,5); 5.39–5.55 (m, 2H, *p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 5.62–5.72 (m, 2H, *p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 6.86 (s, 2H, $NCH_2C_6H_2(CH_3)_3$-2,4,6); 6.18 (d, J = 8.4 Hz, 1H, NC_6H_4N); 6.94–7.04 (m, 2H, NC_6H_4N); 7.30 (d, J = 8.4 Hz, 1H, NC_6H_4N); 6.76–6.81 (m, 3H, $NCH_2C_6H_3(C(CH_3)_3)$-3,5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.7 and 17.2 ($NCH_2C_6H_2(CH_3)_3$-2,4,6); 18.5 (*p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 22.5 (*p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 30.9 (*p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 31.4 ($NCH_2C_6H_3(C(CH_3)_3)$-3,5); 34.9 ($NCH_2C_6H_3(C(CH_3)_3)$-3,5); 52.6 ($NCH_2C_6H_2(CH_3)_3$-2,4,6); 53.5 ($NCH_2C_6H_3(C(CH_3)_3)$-3,5); 84.5, 85.4, 96.1, and 106.9 (*p*-$(CH_3)C_6H_4(CH(CH_3)_2)$; 111.2, 111.8, 119.7, 120.7, 122.3, 122.6, 129.4, 132.7, 133.7, 135.0, 135.5, 135.6, 136.9, and 151.4 (NC_6H_4N, $NCH_2C_6H_3(C(CH_3)_3)$-3,5 and $NCH_2C_6H_2(CH_3)_3$-2,4,6); 189.8 (Ru-carbene); m.p. = 202–203 °C, $\nu_{(CN)}$ = 1436 cm^{-1}, yield 72%. Anal. Calcd for $C_{42}H_{54}N_2RuCl_2$: C: 66.47; H: 7.17; N: 3.69. Found C: 66.45;

H: 7.21; N: 3.70%.

4.3. General procedure for ruthenium NHC catalyzed alkylation of cyclic amines

To a stirred solution of cyclic amine (2.0 eq.) in 1 mL of toluene was added D-(+)-Comphor sulfonic acid (10 mol %). Subsequently aldehyde 1.0 (eq.) and ruthenium catalyst (2.5 mol%) were added and then reaction mixture was stirred at 150 °C for 16 h. After that the schlenk tube was cooled down and then HCOOH (1.5 eq.) was added and stirring continued at 150 °C for 1 h. The crude mixture was directly taken for GC analysis folloed by evaporation of the solvent and the crude mixture was purified by column chromatography(EtOAc/PE; Acetone/Hexane; EtOAc/Hexane) to afford the alkylated cyclic amine as oil. Product was determined by ^{1}H NMR spectroscopy and GC and GC–MS.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.10.011.

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