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Benzimidazolin-2-ylidene *N*-Heterocyclic Carbene Complexes of Ruthenium as a Simple Catalyst for the *N*-Alkylation of Amines using Alcohols and Diols

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Simple air- and moisture stable ruthenium complexes **1-3** and **3a** were synthesized from readily available benzannulated *N*-heterocyclic carbene ligands (bimy = benzimidazolin-2-ylidene). These complexes were found to be efficient catalysts for the alkylation of amines using alcohols as alkylating agents. Catalysts **1**, **2** and **3a** gave excellent yields of up to 99% for the alkylation of various amines using benzylic and aliphatic alcohols at 130 °C for 18 h under solventless conditions. Catalyst **3a** bearing both phosphine and carbene ligands gave excellent yields of up to 98% for the synthesis of heterocyclic amines by double alkylation of primary amines using linear diols. The practical utility of these catalysts were demonstrated for the synthesis of pharmaceutically important amines in a more environmentally benign way under solventless conditions.

Introduction

Molecules that contain C–N bonds are key intermediates in the synthesis of bioactive molecules and play an important role in pharmaceutical industry.[1] Traditional methods for C-N bond formation including S_N2 type amination using toxic alkyl halides[2] and reductive amination using stoichiometric amounts of reducing agents[3] are not environmentally benign or atom economical.[4] Recently, transition metal catalyzed C–N bond formation from alcohols and amines following the so-called "hydrogen borrowing" methodology,[5] has attracted much attention. Alcohols are often low-cost, less hazardous and commercially available starting materials, and water is the only by-product of this reaction, which makes this method environmentally attractive.[6] Pioneering works in this field have been done by the groups of Grigg[7] and Watanabe.[8] Great contributions have also been made by the groups of Crabtree,[9] Williams,[10] Milstein,[11] Beller[12] and Fujita.[13] In most of the cases, Ruthenium[14] or Iridium[15] complexes have been used as catalysts to achieve efficient *N*-alkylation of a variety of amines or ammonia with primary or secondary alcohols including diols. In recent years, catalysts based on other noble metals such as Au,[16] Ag,[17] Os,[18] Rh,[19] and Pd[20] as well as non-noble metals such as Fe,[21] Cu,[22] Ni,[23] Bi,[24] In[25] and Re[26] were also reported to be effective as catalysts for the use of alcohols as *N*-alkylating agents adopting hydrogen borrowing strategy.

N-heterocyclic carbenes (NHCs) have become ubiquitous ligands for homogeneous catalysis,[27] and NHC complexes of ruthenium and iridium have been reported to be active catalysts for the activation of alcohols by hydrogen borrowing strategy. As an early example, Cp*-functionalized iridium-carbene complexes have been reported[28] by Peris *et al.* for the alkylation of aniline and *β*-alkylation of secondary alcohols. Up to 87% of yield was observed in the presence of strong bases such as ^{t}BuOK (110 mol%) at 110 °C. Subsequently, they also reported[29] the application of imidazolin-2-ylidene, imidazolin-4-ylidene and pyrazolin-3-ylidene derived ruthenium complexes as catalyst for the *β*-alkylation of secondary and primary alcohols. In the presence of one equivalent of KOH, quantitative yield of the *β*-alkylated alcohols were formed in toluene at 110 °C. Crabtree *et al.*[9a] reported chelating pyrimidine-NHC complexes of iridium and ruthenium as effective catalysts for the alkylation of amines and secondary alcohols. Using these catalysts, *N*-alkylation of both electron deficient and electron rich amines was carried out in the presence of $NaHCO_3$ (50 mol%) to give the corresponding secondary amines in 25–98% yield. Recently, Valerga *et al.*[30a] reported the *N*-alkylation of both aromatic and non-aromatic amines using Ru(II)-Picolyl-NHC complex[30b] as a catalyst. Turn over numbers (TON) of up to 480 were reported in the presence of 50 mol% of KOH at 100 °C.

Bifunctional Ir catalysts bearing alcohol/alkoxide tethered NHC have been reported for N-alkylation of various amines at temperature as low as 50 °C.[15c] The catalysts were reported to have the ability to accept both proton and the hydride in order to form the products in 77-99% yield in the absence of any external base. Anderson *et al.* reported Ir complexes of

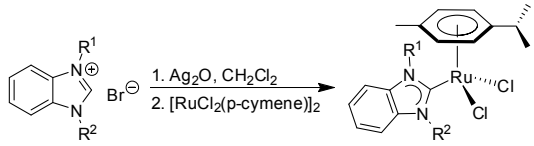
chelating ligand containing phosphine and NHC moiety as catalysts for N-monoalkylation of amines.[15m] Notably, the catalyst promoted the alkylation at 50 °C and at room temperature for selected substrates, in the presence of 50 mol% of ^{t}BuOK to give the alkylated products in 63-97% yields.

To the best of our knowledge, only imidazolin-2-ylidene[29] based complexes having chelating *N*-pyrimidyl[9a] or *N*-picolyl[30] substituents have been reported for the *N*-alkylation of amines, while simpler non-chelating or benzimidazolin-2-ylidene based ruthenium complexes have not been explored yet. Herein, we report simple and non-chelating Ru(II)-NHC complexes of the general formula $[RuCl_2(p\text{-cymene})(bimy)]$ (bimy = benzimidazolin-2-ylidene) as efficient catalysts for the *N*-alkylation of amines using alcohols.

Results and discussion

The preparation of complexes $[RuCl_2(p\text{-cymene})(^iPr_2\text{-bimy})]$ (**1**) and $[RuCl_2(p\text{-cymene})(Bn_2\text{-bimy})]$ (**3**) bearing symmetrical benzimidazolin-2-ylidene ligands were reported previously.[31] Their preparation is improved in this work, and in analogy, the new complex $[RuCl_2(p\text{-cymene})(^iPr,Bn\text{-bimy})]$ (**2**) containing an unsymmetrically substituted NHC was readily synthesized by treating the $[RuCl_2(p\text{-cymene})]_2$ dimer directly with the corresponding Ag-carbene species, that in turn was generated *in situ* by mixing the known benzimidazolium salt **B**[32] with Ag_2O in CH_2Cl_2 (Scheme 1).

Scheme 1. Synthesis of Ruthenium NHC complexes 1–3



A: $R^1 = R^2$ = Isopropyl
B: R^1 = Isopropyl, R^2 = Benzyl
C: $R^1 = R^2$ = Benzyl

1: $R^1 = R^2$ = Isopropyl (58%)
2: R^1 = Isopropyl, R^2 = Benzyl (70%)
3: $R^1 = R^2$ = Benzyl (81%)

In terms of stereoelectronic properties, complex **2** represents a midway between complexes **1** and **3**.[32] Pure samples can be obtained by washing the crude products with water and diethyl ether. The yields of complexes **1**, **2** and **3** were 58%, 70% and 81%, respectively. Notably, the reaction for the preparation of complex **1** is more sluggish than that for complex **2** and **3**. About 20% of unreacted Ru dimer can still be observed by ^{1}H NMR analysis after 12 h. The lower acidity of the C2-H proton in precursor **A** as a consequence of the positive inductive effects from two *N*-isopropyl substituents makes the generation of the required silver carbene species comparatively more challenging. Furthermore, the bulkier isopropyl groups in precursor **A** could also slow down the carbene transfer rate from the Ag complex to the Ru dimer.

Complexes **1**–**3** are soluble in most organic solvents, such as CH_2Cl_2, $CHCl_3$, MeOH and CH_3CN, with the exception of nonpolar ones, such as hexane and diethyl ether. Their formation is supported by ESI mass spectra, where base peaks corresponding to the $[M - 2Cl + OH + MeCN]^+$ fragment were observed. In the ^{1}H NMR spectra, the absence of downfield signals characteristic for the benzimidazolium salts indicates the formation of the expected Ru-NHC complexes. The carbene signals in the ^{13}C NMR spectra of complexes **1**–**3** are observed at 187.4, 189.5 and 191.6 ppm, respectively, which are more downfield compared to their imidazolin-2-ylidene analogues (ca. 170 ppm).[33] The gradual downfield shifts of the $^{13}C_{carbene}$ signals in these three complexes is reflective of the decreasing *+I* effect of the wing tip *N*-substituents on the carbene ligands.

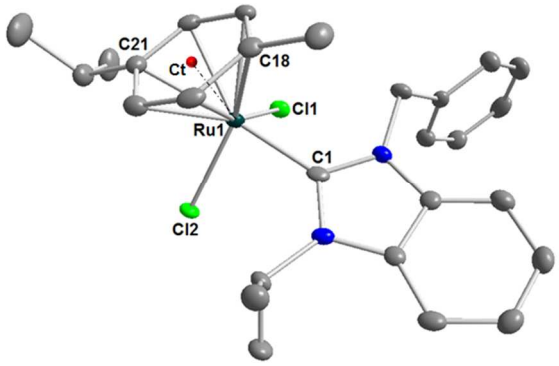


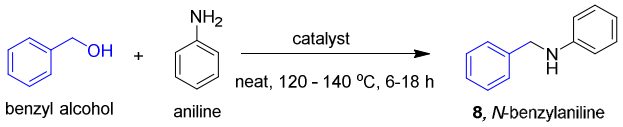
Fig. 1. Molecular structure of complex **2** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ru1–C1 2.0692(24), Ru1–Cl1 2.4096(10), Ru1–Cl2 2.4381(9); Ru1–Cl18 2.2073(24), Ct–Ru1 1.693; Ru1–Cl21 2.2638(26); Cl1–Ru1–Cl2 83.795(2), Cl1–Ru1–C1 89.200(6), Cl2–Ru1–C1 91.721(7).

The molecular structure of **2** (Fig. 1) was determined by X-ray diffraction on single crystals obtained by diffusion of diethyl ether into a dichloromethane solution. This complex adopts three-legged piano stool geometry with the facial planar *p*-cymene representing the "seat", and the two chlorido and one NHC ligands form the three "legs". Although the carbon atom C21 is situated "transoid" to the carbene donor C1 (C21–Ru1–C1 = 162.13°), no trans influence from the NHC ligand can be discerned as all Ru-C_{cymene} bonds are of essentially the same length within 3σ with an average value of 2.209 Å. The Ru-centroid distance amounts to 1.693 Å. Both the *N*-benzyl group and the *N*-isopropyl group are pointing away from the Ruthenium center to avoid steric repulsion, and the bulkier isopropyl group in the *p*-cymene ring is also oriented away from the benzimidazolin-2-ylidene ligand for the same reason.

The catalytic activity of the ruthenium benzimidazolin-2-ylidene complexes **1** – **3** for alcohol activation towards *N*-alkylation was investigated by taking the coupling between benzyl alcohol and aniline as a standard reaction (Table 1). Catalyst **1** having the NHC ligand symmetrically substituted with isopropyl group was selected for initial optimization of the reaction conditions. Only a moderate 40% yield (entry 1) of the *N*-benzylamine product was obtained after 18 h at a lower catalyst loading of 1.0 mol% and at a reaction temperature of 130 °C under solventless conditions. The yield increased to 70% upon increasing the amount of the catalyst to 2.5 mol% (entry 2). Increase in temperature showed no significant improvement (entry 3), but the yield decreased when the temperature was lowered (entry 4).

In general, the initial catalytic activity observed was higher and up to 60% yield was obtained for a 6 h reaction at 130 °C (entry 5). Under these conditions, doubling the catalyst loading improved the yield to 80% (entry 6). At this point, the catalytic performance in presence of a solvent was investigated. The catalytic performance decreased drastically, and only 13% and 8% yields were observed with common solvents generally used for this reaction such as toluene and diglyme (entries 7 & 8), respectively.

Table 1: Optimization of catalyst and reaction conditions[a]



benzyl alcohol aniline **8**, *N*-benzylaniline

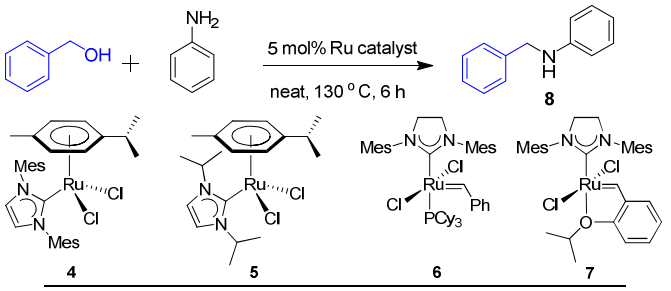
entry	catalyst	amount of catalyst (mol%)	temp. (°C)	time (h)	yield, (%)
1	**1**	1.0	130	18	40
2	**1**	2.5	130	18	70
3	**1**	2.5	140	18	68
4	**1**	2.5	120	18	53
5	**1**	2.5	130	6	60
6	**1**	5.0	130	6	80
7	**1**	5.0	130	6	13[b]
8	**1**	5.0	130	6	8[c]
9	**2**	5.0	130	6	62
10	**3**	5.0	130	6	5
11	**1**	5.0	130	18	>99
12	**2**	5.0	130	18	>99

[a] Reaction conditions: 1 mmol of aniline, 1.2 mmol of benzyl alcohol. % yields were determined by GC analysis using docecane as the internal standard. [b]Toluene as solvent, [c]Diglyme as a solvent.

Under the present optimized conditions, catalyst **2** having one of the isopropyl substituents replaced with a benzyl group gave a yield of 62% (entry 9). However, the catalytic activity was nearly suppressed when both the isopropyl groups were replaced with benzyl groups as in catalyst **3**. The unfavorable effect of the benzyl groups on the catalytic performance may be due to a possible π-coordination[34] of benzyl moiety to the Ru-center upon removal of *p*-cymene or other ligands under the reaction conditions, thus hindering the coordination and further activation of substrates and intermediates. Although catalyst **2** shows slightly lower initial activity compared to **1**, both the catalysts (**1** and **2**) gave near quantitative yields upon increasing the reaction time to 18 h (entries 11 & 12).

The catalytic performances of the benzimidazolin-2-ylidene ruthenium complexes **1** – **3**, were compared with those of some common ruthenium imidazolin- and imidazolidin-2-ylidene complexes (**4** – **7**) under the same optimized conditions, and the results are given in Table 2. Complexes **4** and **5** with IMes and I^{i}Pr ligands gave lower yields of 24% and 19% (entries 1 & 2), respectively. Grubb's second generation catalyst (**6**) bearing the SIMes gave an improved yield of 88% while, the Hoveyda-Grubb's catalyst (**7**) gave up to 74% yield (entries 3 & 4). We reckoned that the improved catalytic performance observed with Grubbs II catalyst **6** compared to other catalysts may be due to the presence of a phosphine (PCy_3) as an additional ligand. Hence, the addition of phosphine was investigated to examine if any beneficial synergistic effect exists. No specific effect was observed with the Hoveyda-Grubb's catalyst (**7**) in the presence of PPh_3.[35] However, enhanced catalytic activity was noted with catalysts **4** and **5**, and up to 51% and 45% yields were observed at 130 °C after 6 h (entries 5 & 6).

Table 2: Catalytic activity of various Ru-NHC complexes[a]

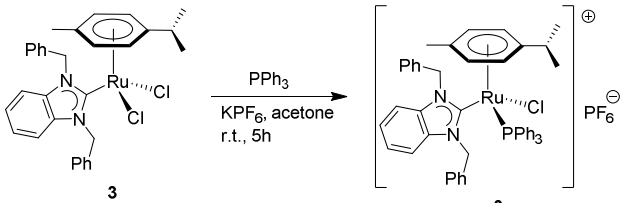


entry	catalyst	additive	yield (%)
1	**4**	Nil	24
2	**5**	Nil	19
3	**6**	Nil	88
4	**7**	Nil	74
5	**7**	PPh_3 (5 mol%)	75
6	**4**	PPh_3 (5 mol%)	51
7	**5**	PPh_3 (5 mol%)	48
8	**1**	PPh_3 (5 mol%)	87
9	**2**	PPh_3 (5 mol%)	64
10	**3**	PPh_3 (5 mol%)	85

[a] Reaction conditions: 1 mmol of aniline, 1.2 mmol of benzyl alcohol. 5 mol% of Ru-NHC catalyst at 130 °C for 6 hrs. % yields were determined by GC analysis using docecane as the internal standard.

The performance of catalysts **1** and **2** marginally improved in the presence of PPh_3 giving up to 87% and 64% yields, respectively (entries 8 and 9). However, the 1,3-dibenzyl-benzimidazolin-2-ylidene complex **3** became much more active in the presence of PPh_3 yielding up to 85% of the product (entry 10). This favorable effect of the phosphine could be due to its coordination to the ruthenium center, which may sterically prevent the π–coordination of benzyl moiety to the Ru-center.

Scheme 2: Synthesis of Ru-NHC-Phosphine complex 3a

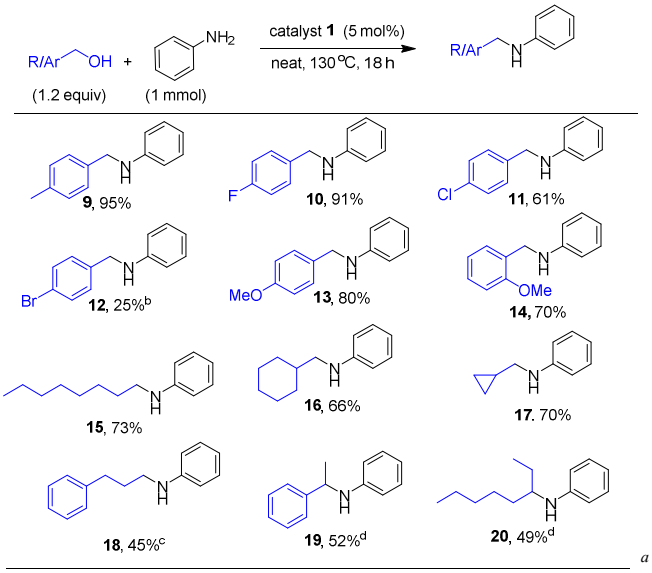


In order to understand this beneficial effect on relatively inactive complexes such as **3**, the new mixed NHC/Phosphine ruthenium complex $[RuCl_2(p\text{-cymene})(bimy)Cl(PPh_3)]PF_6$ (**3a**) was prepared as shown in Scheme 2 for the purpose of further comparison. A small improvement in catalytic activity was

observed (87%, under the reaction conditions given in Table 2) with well-defined **3a** compared to that of the in-situ generated species by external addition of PPh_3 to catalyst **3** (85%, Table 2, entry 10). Notably, near quantitative yield was observed for **3a** upon increasing the reaction time to 18 h. Since the benzimidazolin-2-ylidene (bimy) complexes **1**, **2** and **3a** gave similar results for the *N*-alkylation using primary alcohols under the optimized conditions (at 130 °C for 18 h under solventless conditions), they were further evaluated for substrate scope and limitations.

Alkylation of aniline using various benzylic and aliphatic alcohols gave good to excellent results using catalyst **1** as presented in Table 3. Excellent isolated yield of 95% was achieved for the secondary amine **9** when *p*-Me substituted benzylalcohol was used as the alkylating agent. *p*-F and *p*-Cl substituted benzyl alcohols gave the corresponding secondary amine products **10** and **11** in 91% and 61% isolated yields respectively. The *p*-Br substituted benzyl alcohol showed poor activity yielding **12** in 25% with lower conversion. Both *p*-OMe and *o*-OMe substituted benzyl alcohols were coupled with aniline giving the corresponding secondary amine products **13** (80%) and **14** (70%) in very good yields. The relatively less reactive aliphatic alcohols were also found to be promising alkylating agents and up to 73% isolated yield of *N*-octyl aniline (**15**) was obtained when 1-octanol was used. Secondary amines such as **16** and **17** were obtained in good yield of 66% and 77% respectively, when cyclohexylmethanol and cyclopropylmethanol were used as the alkylating agents. Aliphatic alcohol such as 3-phenylpropanol gave only moderate yield of 45% of the secondary amine **18** under the present set of conditions. Secondary alcohols such as 1-phenylethanol and 2-octanol were found to be poor alkylating agents in the presence of catalyst **1**, **2** and **3a** providing maximum yields of 52% (**19**) and 49% (**20**).

Table 3. Alkylation of aniline using various alcohols[a]

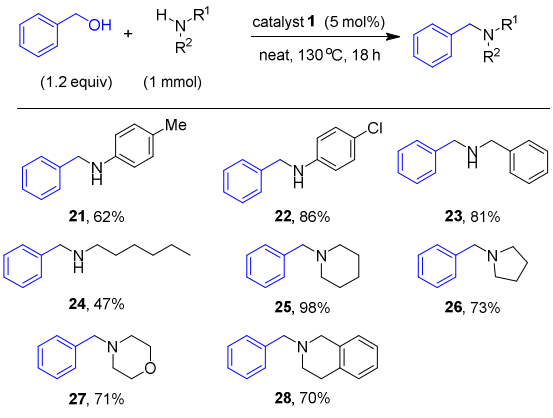


[a] Reaction conditions: 1 mmol of aniline, 1.2 mmol of alcohol, 5 mol% of catalyst **2** at 130°C for 18h. Isolated yields are given. [b] **2** was used as the catalyst; catalysts **1** and **3a** gave 18% and 22% yields respectively. [c] **2** was used as the catalyst; catalysts **1** and **3**a gave 40% and 43% yields respectively. [d]Catalyst **3a** was used, catalysts **1** and **2** gave lower yields.

Next, the substrate scope of amines was investigated using benzyl alcohol as the alkylating agent (Table 4). Electron donating *p*-Me substituted aniline gave **21** in moderate yield of 62%, while an increased yield up to 86% was observed for **22** when *p*-chloro aniline was used as the substrate. Benzylamine gave dibenzylamine (**23**) in 81% yield, whereas 47% yield of the secondary amine **24** was observed when an aliphatic amine such as hexylamine was used. Near quantitative yield of the tertiary amine **25** was achieved for the alkylation of six membered cyclic amine such as piperidine. Other cyclic amines such as pyrrolidine, morpholine and 1,2,3,4-tetrahydroisoquinoline were also readily alkylated giving the corresponding cyclic tertiary amines **26** – **28** in 70 – 73% isolated yields.

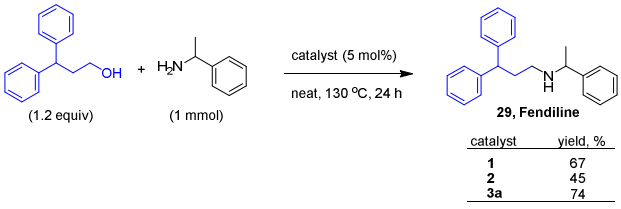
The possible application of the benzimidazolin-2-ylidene complexes **1**, **2** and **3a** were further examined for the synthesis of pharmaceutically important secondary and tertiary amines. For this purpose, Fendiline (**29**), an anti-anginal agent was chosen as an initial example (Scheme 3). The direct synthesis of Fendiline[36] was reported previously by Williams and coworkers adopting hydrogen borrowing strategy in presence of $[Cp^*IrCl_2]_2$ as the catalyst. [37]

Table 4. Alkylation of various amines using benzyl alcohol[a]



[a] Reaction conditions: 1 mmol of amine, 1.2 mmol of benzyl alcohol, 5 mol% of catalyst **1** at 130 °C for 18 h. Isolated yields are given.

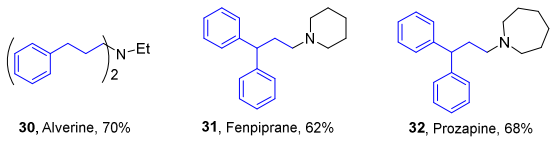
Scheme 3: Catalyst optimization for the synthesis of Fendiline



catalyst	yield, %
1	67
2	45
3a	74

Catalyst **1** having symmetrically substituted isopropyl groups gave up to 69% yield, while the unsymmetrically substituted catalyst **2** gave a lower yield of 43% at 130 °C after 24 h reaction. Interestingly, catalyst **3a** gave an improved yield of 74% and was selected for further applications in the synthesis of pharmaceutically important amines. Under the standardized conditions as shown in Scheme 3, good isolated

yield of 62 – 70% were achieved for the synthesis of some of the pharmaceutically important compounds such as Alverine[38] (**30**), Fenpiprane[39] (**31**) and Prozapine[39] (**32**) (Fig. 2). To the best of our knowledge, H-borrowing strategy has not been demonstrated for the synthesis of pharmaceutically important molecules **30**-**32**.

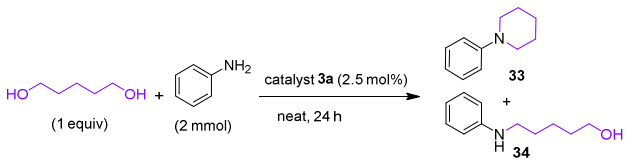


30, Alverine, 70% **31**, Fenpiprane, 62% **32**, Prozapine, 68%

Fig. 2: Synthetic application of catalyst 3a for the preparation of pharmaceutically important amines.

The cyclization using diols following hydrogen borrowing strategy is a convenient protocol to prepare several value-added cyclic amines from the corresponding primary amines. Yamaguchi *et al*. employed iridium catalyst for the synthesis of cyclic tertiary amines by reaction of various primary amines with suitable diols to achieve good yields.[40] Ruthenium catalysts were reported to be effective for using diols as alkylating agents for the preparation of cyclic amines.[10a,41] Considering the importance of cyclic amines, we have investigated the catalytic performance of the benzannulated NHC complexes **1, 2** and **3a** for their synthesis using diols as alkylating agents.

Table 5. Optimization of *N*-alkylation using diols[a]



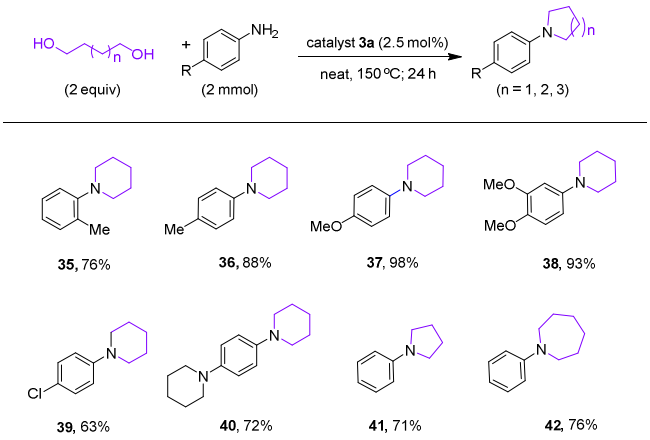
entry	catalyst	temp. (°C)	conv. (%)	yield of **33** (%)	yield of **34** (%)
1	**1**	130	89	33	55
2	**2**	130	82	23	58
3	**3a**	130	96	66	29
4	**3a**	150	98	93[b]	4
5	**1**	150	87	47	38
6	**2**	150	86	45	39

[a] Reaction conditions: 2 mmol of aniline, 2 mmol of 1,5-pentanediol. 2.5 mol% of Ru-NHC catalyst for 24 h. Yields were determined by GC analysis using dodecane as the internal standard. [b] 89% isolated yield

As shown in Table 5, yields of 23 - 33% were observed for the cyclized product *N*-phenyl piperidine (**33**) with a conversion of 89% at 130 °C after 24 h using 2.5 mol% catalysts **1** and **2**. In both the cases, the monoalkylated product **34** was found to be the major product (entries 1 & 2). However, up to 66% yield to **33** was observed with the catalyst **3a**, which was further improved to 93% (entry 4) upon increasing the temperature to 150 °C. No specific temperature effect was observed for the catalyst **1** or **2**. This optimized condition was used to extend the substrate scope using various diols as alkylating agents for the synthesis of cyclic amines.

Excellent yields up to 98% were achieved for various anilines as substrates at 150 °C as given in Table 6. Both *o*-Me and *p*-Me substituted anilines were double alkylated with 1,5-pentandiol giving the cyclized product **35** and **36** in 76% and 88% yields, respectively. Excellent yields were also achieved for the synthesis of **37** (98%) and **38** (93%) using 4-methoxy and 3,4-dimethoxy substituted anilines. 1-(4-chlorophenyl)piperidine (**39**) was obtained in 63% yield from 4-chlorophenyl aniline and 1,5-pentandiol. 1,4-di(piperidin-1-yl)benzene (**40**) was obtained in 73% yield from 4-(piperidin-1-yl)aniline and 1,5-pentanediol. Both 1,4-butanediol and 1,6-hexandiol react smoothly with aniline to form 1-phenylpyrrolidine (**41**) and 1-phenylazepane (**42**), respectively, in very good yields.

Table 6. Synthesis of various cyclic amines by *N*-alkylation using diols[a]



[a] Reaction conditions: 2 mmol of aniline, 2 mmol of diol, 150 °C, 24h. 2.5 mol% of Ru-NHC catalyst for 24 h. Isolated yields are reported.

Ruthenium catalyzed alcohol activation is reported to proceed through the formation of a Ru-H species as an active intermediate that initiate the catalytic cycle.[42] In the present Ru-NHC catalyst system, formation of a Ru-H species[43] at δ = -9.62 ppm was detected by ^{1}H NMR spectroscopy (Fig. 3, spectrum **A**) from an intermediate reaction sample after 2 h of the standard *N*-alkylation reaction[44] (Table 1) at 100 °C using catalyst **1**. Apart from this signal, additional signals at -1.69 and -2.93 ppm were also observed. In the presence of one additional equivalent of PPh_3,[44] two doublets at -7.36 (J = 53.4 Hz) and -9.41 ppm (J = 56.2 Hz) as well as two triplets at -9.81 (J = 35.8 Hz) and -13.28 ppm (J = 19.9 Hz) were observed[45] showing the formation multiple Ru-H species coordinated with PPh_3 (Fig. 3, Spectrum **B**). The nearly inactive complex **3** showed one prominent Ru-H signal at -8.3 ppm along with a slightly upfield shifted, low intensity broad resonance (Fig. 3, Spectrum **C**), which may be attributed to a possible formation of stable π-benzyl coordinated species that may restrict coordination of the intermediate imine for completing the catalytic cycle. However, in the presence of added one equivalent of PPh_3, this Ru-H species was considerably reduced with the formation of three sets of doublets (δ = -9.09, -9.82 and -10.01; approx. J = 48 Hz) and two sets of triplets (δ = -9.81 and -10.88; J = 35.7 Hz) (Fig. 3, Spectrum **D**). Some of these hydride signals were found to disappear with time.

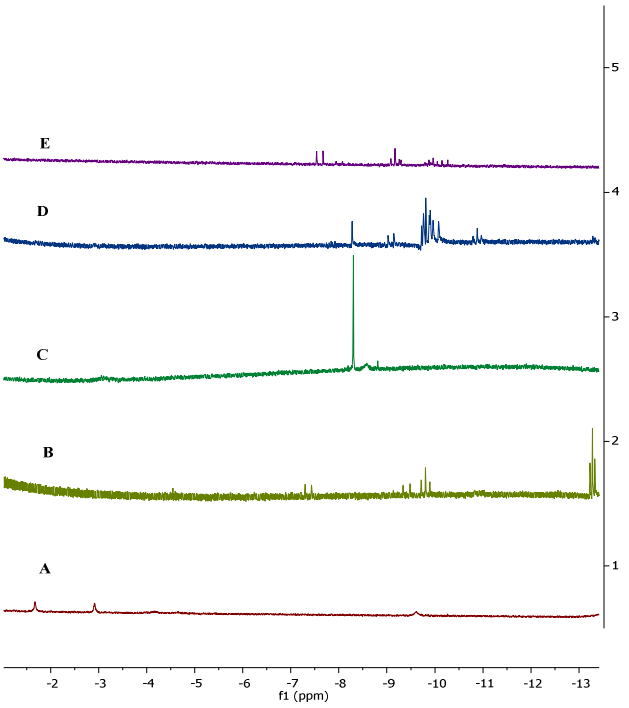


Fig. 3. ^{1}H NMR spectroscopic (400 MHz) analysis for Ru-H species formed under reaction conditions with Complex **1** (A, $CDCl_3$), Complex **1**+PPh_3 (B, $CDCl_3$), Complex **3** (C, $CDCl_3$), Complex **3**+PPh_3 (D, $CDCl_3$) and Complex **3a** (E, DMSO-d_6).[44]

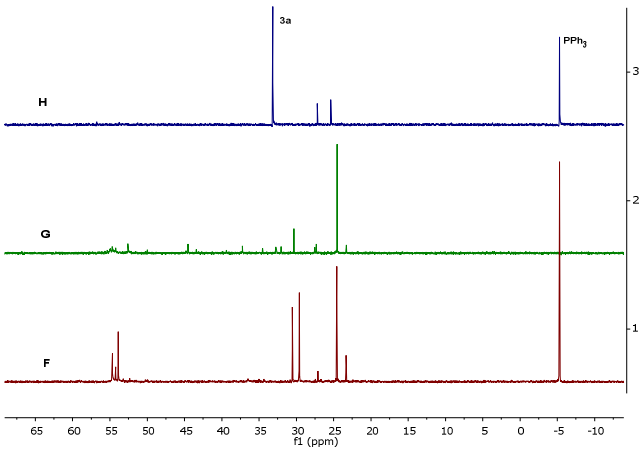
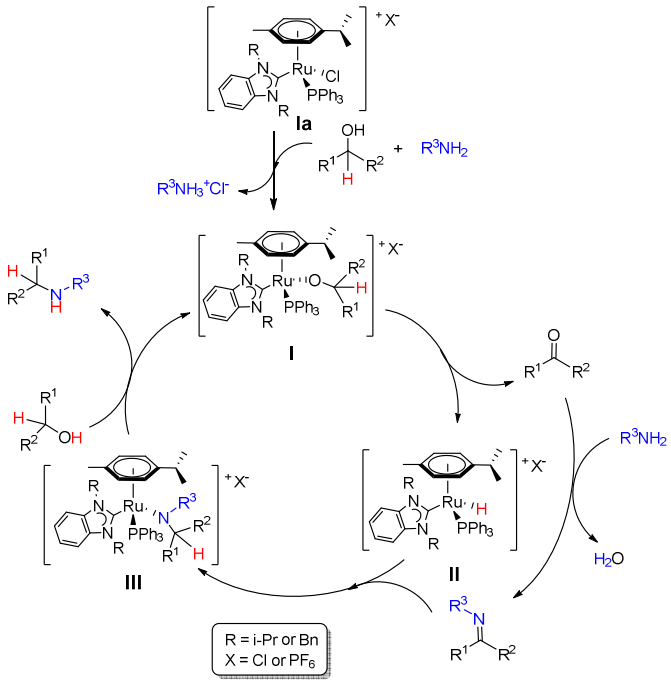


Fig. 4. $^{31}P\{^{1}H\}$ NMR spectroscopic analysis (162 MHz) for intermediate Ru species formed under reaction conditions with Complex **1**+PPh_3 (H, $CDCl_3$), Complex **3**+PPh_3 (G, $CDCl_3$) and Complex **3a** (F, DMSO-d_6)

Unfortunately, the intermediate complexes obtained from **3a** were not very stable and immediately precipitated as the parent compound **3a** upon dissolving in common deuterated solvents ($CDCl_3$, CD_3OD, etc.). However, from a dilute solution obtained by warming the reaction mixture in DMSO-d_6, we could observe multiple Ru-H signals (Fig. 3, Spectrum **E**) such as three doublets {-7.61 ppm, (J = 47.3 Hz), -8.01 ppm (d, J = 52.1 Hz and -10.28 ppm (d, J = 48.3 Hz)}, one triplet at -10.28 ppm (d, J = 48.3 Hz); and one doublet of doublet at -9.18 ppm (J = 49.2, 13.4 Hz). In all these cases two to four sets of *p*-cymene signals[44] were also detected showing the presence of coordinated *p*-cymene ligand in these intermediate complexes.

In an effort to further characterize the intermediates, $^{31}P\{^{1}H\}$NMR analysis (Fig 4) was carried out with the samples obtained under reaction conditions from complexes **1**+PPh_3 (Spectrum **F**), **3**+PPh_3 (Spectrum **G**) and **3a** (Spectrum **H**). In the case of **3a**, two new species were detected at 27.18 and 25.39 ppm together with free PPh_3 (-5.29 ppm) and **3a** (33.17 ppm). Complex **3** in the presence of added PPh_3 gave a major signal at 24.52 ppm and several ^{31}P NMR signals in the range of 20 to 55 ppm, which were difficult to assign to any particular intermediate species. However, complex **1** with added PPh3 gave five sharp signals in the range of 25 to 55 ppm with a major signal at 24.56 ppm. The signal at 24.5 ppm in both these cases can be assigned to a phosphine coordinated precatalyst such as [$RuCl_2$(NHC)(PPh_3)(p-cymene)], similar to species **Ia** in Scheme 2. The other signals may correspond to various phosphine-coordinated Ru species including that of ruthenium-hydrido intermediates.

Scheme 2: Proposed catalytic cycle



Based on the detection of various Ru-H species and Ru-P species as well as other literature reports[42] we are proposing a simple catalytic cycle as shown in scheme 3 likely involving a Ru-alkoxide complex **I** formed from the phosphine coordinated Ru-NHC pre-catalyst upon reaction with the alcohol, as the active catalytic species initiating the catalytic cycle. The Ru-complex **I** is transformed to a possible Ru-H complex **II** by elimination of the carbonyl intermediate, which condenses with the amine to form the imine intermediate. Insertion of this imine intermediate into the Ru-H species **II** generates the Ru-complex **III**, which produces the amine product and the active complex **I** upon subsequent reaction with the alcohol. PPh_3 is optionally coordinated and in its absence, a corresponding neutral Ru-Cl complex or cationic complex with a vacant coordination site can be envisaged. Notably, all proposed catalytic intermediates are chiral-at-metal. In combination with

the planar chirality resulting from restricted rotation of the *p*-cymene ligand, diastereomeric mixtures can be anticipated, which also explains the multiple species noted in Figure 3 and 4. A detailed analysis, both experimental and theoretical calculations, is required to understand the exact nature of the various ruthenium intermediates formed under the reaction conditions to validate this proposed mechanism and is currently in progress at our laboratory .

Conclusions

In conclusion, we have reported the synthesis of ruthenium complexes bearing symmetrically (**1**, **3** and **3a**) and unsymmetrically (**2**) substituted benzimidazolin-2-ylidene ligands. These ruthenium-NHC complexes showed promising catalytic activity for the alkylation of various amines using alcohols under solvent-free conditions in the absence of any external base. The catalysts were shown to be effective for the synthesis of pharmaceutically important amines such as Fendiline, Alverine, Fenpiprane and Prozapine giving generally very good yields. Five- to seven-membered *N*-heterocyclic amines were synthesized expediently from the corresponding diols using the cationic Ru catalyst **3a** having both phosphine and carbene ligands. In general, the initial catalytic activity was found to be in the order **3a** > **1** > **2** >>> **3**. The robustness of these benzimidazolin-2-ylidene ruthenium complexes, their easy accessibility and wide applicability make them attractive catalysts for the synthesis of various important amines through alkylation using alcohols following hydrogen borrowing strategy. A catalytic cycle initiated by a Ru-alkoxide species is proposed based on the detection of Ru-H species by ^{1}H and ^{31}P NMR spectroscopic analysis.

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Simple non-chelating ruthenium benzimidazolin-2-ylidene complexes as efficient *N*-alkylation catalyst using alcohols and diols following hydrogen borrowing strategy.