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Amination of aliphatic alcohols with urea catalyzed by ruthenium complexes: effect of supporting ligands

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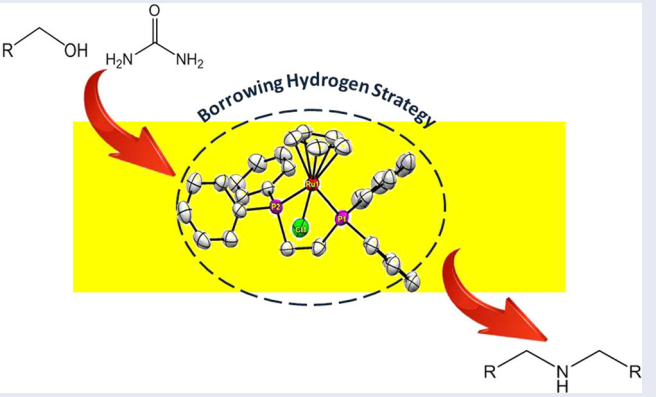
ABSTRACT

In the present study, ruthenium-catalyzed amination of alcohols by urea as a convenient ammonia carrier in the presence of free diphosphine ligands has been described. A number of ruthenium-phosphine complexes have been studied among which, [(Cp)RuCl(dppe)] was found as an efficient catalyst for alcohol amination reaction. The crystal structures of two new half-sandwich ruthenium complexes, [(Cp)RuCl(dppe)] and $[(C_6H_6)RuCl_2(PHEt_2)]$, were determined by X-ray crystallographic analysis. Also the effect of using different supporting phosphines, ratio of raw materials and reaction temperature on conversion and selectivity was investigated. Under optimum reaction conditions high conversion (98%) and chemo-selectivity toward secondary amines were obtained.



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KEYWORDS
Amination reaction; urea; half-sandwich ruthenium complex; diphosphine ligands; homogeneous catalyst; borrowing hydrogen method

1. Introduction

Amines are essential intermediates in large scale production of industrial chemicals. Lower aliphatic amines (C_1–C_6) are important intermediates in chemical, pharmaceutical and petrochemical industries and have many applications as corrosion inhibitors in lubricating oils, greases and fuel oil as sludge dispersants and stabilizers [1, 2].

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Higher aliphatic amines (fatty amines) and their derivatives also are useful as fabric softeners, corrosion inhibitors and emulsifiers [3]. The most significant method known for production of aliphatic amines is the reductive amination of the corresponding carbonyl compounds [4, 5]. Utilizing stoichiometric amounts of toxic and expensive reagents, low selectivity, low atom-economy and large amounts of wasteful salts have been recognized as the main problematic issues in these reactions [6–8]. Given this drawback as well as the benefits which could be brought up with green chemistry, the development of methods which are economically and environmentally accepted and more efficient for the synthesis of amines is still a challenge for researchers to be taken into account. A green approach of catalytic alkylation of amines using alcohols instead of aldehydes or ketones has been done via a facile strategy known as "Borrowing Hydrogen" method which is an attractive candidate for synthesis of amines since alcohols are inexpensive, readily available, non-toxic and theoretically water is the only by-product [9, 10]. The Borrowing Hydrogen, also called hydrogen auto-transfer, catalytic cycle involves initial metal catalyzed dehydrogenation to form an intermediate carbonyl compound which undergoes condensation with the amine to form corresponding imine and water. Hydrogen generated in the dehydrogenation step reduces the imine to reach the desired alkylated amine product [11].

Reactions of simple alcohols (e.g. methanol and ethanol) with ammonia are used for commercial production of amines in the presence of heterogeneous catalysts, severe reaction conditions (relatively high temperatures and pressures), also lower selectivity is consequences of utilizing these types of catalysts [12]. The first homogeneously catalyzed reaction of this type was reported by Grigg and Watanabe in 1981 [13, 14], in which a number of examples have been catalyzed by mainly ruthenium- and iridium-based complexes and less commonly by other transition metal complexes. The scope of ruthenium-catalyzed Borrowing Hydrogen amination could be significantly improved by the development of catalyst systems that require lower catalyst loading, shows broader substrate scope, avoid the need for a large excess of either the alcohol or the amine and operate at more moderate temperatures and with shorter reaction times [15]. Recently, great contributions have also been made by the groups of Beller [16, 17], Williams [18, 19], Milstein [20], Zhao [21], Fujita [22] and Bruneau [23]. Catalytic systems based on ruthenium precursors have proved to be efficient for N-alkylation of amines by alcohols in the preparation of higher amines. Despite the recent progress in catalytic aminations, the chemo-selective synthesis of amines using ammonia is a highly challenging goal. Owing to their nucleophilicity, primary amines are in general more reactive than ammonia, and the sequential formation of secondary and tertiary amines results [24]. Although low cost and convenient availability of ammonia make it a proper source of nitrogen, there are some difficulties regarding its storage, handling and transportation. Applying ammonium related compounds such as ammonium salts or urea are an attractive alternative to tackle these issues [25, 26]. Despite its great potential to synthesize amines by reaction with alcohols, there are only several reports in the literature, for example, synthesis of secondary and tertiary amines from NH_4OAc and NH_4BF_4 have been reported by a homogenous iridium (Cp^*Ir) catalyst [27, 28]. Urea as abundant and inexpensive material that provides high nitrogen content can be used for preparation of valuable

nitrogen containing compounds. In 2009, synthesis of tertiary and secondary amines directly from alcohols and urea was reported by Mizuno [29]. However, $Ru(OH)_x/TiO_2$ performed as an efficient heterogeneous catalyst; obtaining of the desired substituted amines required large excess of alcohols (alcohol/urea = 10:1). Cao *et al.* obtained the best activity and selectivity for preparation of tertiary amine using an expensive gold catalyst (Au/TiO_2) [30].

In this article, half-sandwich ruthenium complexes have been synthesized and tested homogeneously for preparation of aliphatic amines from different linear aliphatic alcohols using urea as nitrogen source. Secondary amines were prepared with acceptable chemoselectivity from several aliphatic alcohols with urea through the use of catalytic amounts of ruthenium complexes. Also the effect of a number of phosphine ligands as supporting ligands on activity and selectivity of the reaction were investigated. Several experiments were performed with different ratios of urea and alcohol to find optimum conditions.

2. Experimental

2.1. Materials and instrumentation

All the used chemicals and reagents in this study were Sigma-Aldrich and StremChemical Companies' products and utilized without purification. The solvents were of analytical grade and purified prior to use based on standard methods. ^1H NMR spectra were recorded at room temperature in $CDCl_3$ on a Bruker Avance 400 MHz instrument. Single-crystal X-ray diffraction data were collected on a MAR345-dtb diffractometer with an image plate detector graphite-monochromated Mo Ka radiation at room temperature using Stoe X-AREA software. A Gas Chromatograph (GC), Agilent Technologies 7890 A Instrument (equipped with a HP-1 capillary column, a FID detector, and a mass spectroscope model 5975 C with a triple-axis detector), were used for monitoring of reaction products and their identity and octane considered as the internal standard. $[(Ru(cymene)Cl_2]_2$, $[RuCl_2(\eta^6\text{–}C_6H_6)]_2$, $[RuH_2(CO)(PPh_3)_3]$, $[RuCl(OAc)(PPh_3)_3]$ and $[(Cp)RuCl(PPh_3)_2]$ were prepared according to literature methods [31–33]. Ruthenium diphosphine complexes were synthesized by published methods [34, 35].

2.2. Catalyst preparation

2.2.1. [(Cp)RuCl(dppe)]

This complex was prepared according to the method reported by Ashby [36]. Diphenylphosphinoethane (dppe) (160 mg, 0.4 mmol) was added to a solution of $[RuCpCl(PPh_3)_2]$ (290 mg, 0.4 mmol) in toluene (50 mL) (Scheme 1, (a)). The mixture was refluxed for 10 h, and then the solution was cooled to room temperature. The solution was then concentrated in vacuum to approximately 1 mL and the product precipitated with diethyl ether. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.14–7.19 (m, 20H, Ph), 4.56 (s, 5H, C_5H_5), 2.41–2.65 (m, 4H, P-CH_2). ^{31}P NMR ($CDCl_3$), δ (ppm): 79.60.

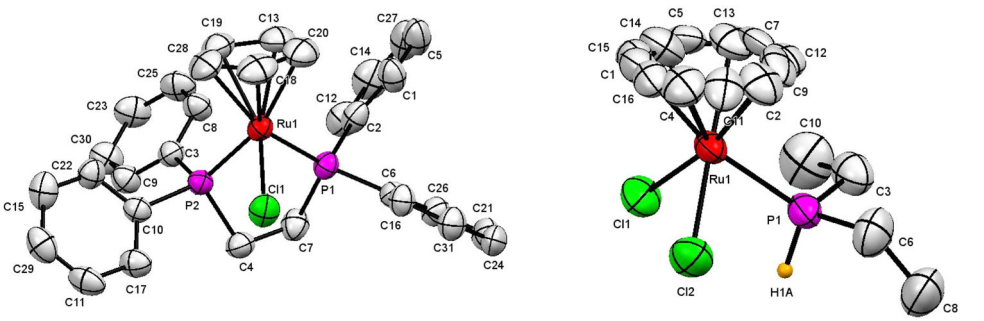


Figure 1. ORTEP view of (A) [(Cp)RuCl(dppe)] (**1**) and (B) [$(C_6H_6)RuCl_2(PEt_2H)$] (**2**) with atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. Orientation disorder was observed for benzene ring in **2** at 298 K. The hydrogen atom attached to P_1 is shown in **2**; all other hydrogens are not shown.

2.2.2. [$(C_6h_6)RuCl_2(PEt_2H)$]

In a 50-mL round bottom flask, 300 mg (0.6 mmol) of $[(C_6H_6)RuCl_2]_2$ was dissolved in 50 mL toluene, then an excess amount of diethylphosphine (PEt_2H) (1 mL) was added to the solution. The reaction mixture was heated under reflux for 8 h (Scheme 1, (b)). The solution was cooled, and the solvent was removed under reduced pressure afterwards, and the residual brown solid was recrystallized from dichloromethane-ether to give red crystals of the complex [37]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.8 (s, 6H, C_6H_6), 4.65 (dm, 1H, H-P, $^1J_{PH}$ 381.2), 2.17 (m, 6H, CH_2), 1.29 (dt, 4H, CH_3). ^{31}P NMR ($CDCl_3$) δ (ppm): 23.03.

2.3. General catalytic procedure for amination

The autoclave was charged with 1-hexylalcohol (2.5 mmol) and urea (2.5 mmol) in 1 mL diglyme. [(Cp)RuCl(dppe)] (3% mol) as catalyst, diphenylphosphinopropane (dppp) (0.07 mmol) as supporting ligand and 0.04 g K_2CO_3 as base was added. The autoclave was closed, flushed with argon for 5 min and then temperature was adjusted at 160 °C. After 12 h, the autoclave was cooled to room temperature and the products were analyzed by gas chromatography.

3. Results and discussion

3.1. Crystal structures

The molecular structures of [(Cp)RuCl(dppe)] (**1**) and [$(C_6H_6)RuCl_2(PHEt_2)$] (**2**) are illustrated in Figure 1. These complexes are air-stable, soluble in most organic solvents and crystallize in the monoclinic space group $P2_1$. Suitable crystals of the complexes were obtained by slow diffusion of diethyl ether in DCM solution of **1** and CH_3CN solution of **2**. The structures of **1** and **2** are similar to previously reported half-sandwich ruthenium(II) complexes and single-crystal structure of complexes confirmed three-legged piano-stool geometry for Ru(II) in both complexes with chlorine and

Table 1. Crystallographic and structure refinement data of **1** and **2**.

	[(Cp)RuCl(dppe)]	[$(C_6H_6)RuCl_2(PEt_2H)$]
Formula	$C_{31}H_{29}ClP_2Ru$	$C_{10}H_{16}C_{l2}PRu$
Fw	600.0	340.17
λ/Å	0.71073	0.71073
T/K	290(1)	290(1)
Crystal system	Monoclinic	Monoclinic
Space group	$P12_11$	$P12_11$
a/Å	9.4949(19)	7.4980(15)
b/Å	15.042(3)	15.538(3)
c/Å	9.983(2)	11.681(2)
α/°	90	90
β/°	110.16(3)	100.969(3)
γ/°	90	90
V/Å^3	1338.4(5)	1336.1(5)
D_{calc}/Mg.m^{-3}	1.489	1.691
Z	2	4
μ (mm^{-1})	0.824	1.656
F(000)	612	680
2θ (°)	52.0	49.962
R (int)	0.0387	0.0566
GOOF	1.093	1.168
R_1[a]($I > 2\sigma(I)$)	0.0328	0.0365
wR_2[b]($I > 2\sigma(I)$)	0.0905	0.0847
CCDC No.	2000008	2000009

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b]$wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)2]^{1/2}$.

Table 2. Selected geometric parameters for **1** and **2**.

Parameters	1	Parameters	2
Bond distances			
$Ru–Cl_1$	2.441	$Ru–Cl_1$	2.401
$Ru–P_1$	2.286	$Ru–Cl_2$	2.416
$Ru–P_2$	2.268	$Ru–P_1$	2.310
$Ru–C_{Cent}$	1.865	$Ru–C_{Cent}$	1.673
		$P_1–C_3$	1.820
Bond angles			
$P_1–Ru–Cl_1$	82.36	$P_1–Ru–Cl_1$	86.86
$P_2–Ru–Cl_1$	84.48	$P_1–Ru–Cl_2$	81.69
$P_1–Ru–P_2$	82.57	$Cl_1–Ru–Cl_2$	87.17
$P_1–Ru–C_{13}$	98.74	$P_1–Ru–C_2$	100.90
$P_2–Ru–C_{19}$	98.87	$P_1–Ru–C_{12}$	87.80
$Cl–Ru–C_{18}$	91.39	$Cl_1–Ru–C_{14}$	90.28
$P_1–C_7–C_4$	111.32	$Cl_2–Ru–C_4$	90.98
$P_2–C_4–C_7$	107.91		

phosphine ligands. Crystallographic data and selected bond lengths and angles are listed in Tables 1 and 2, respectively.

Complex **1** consists of one bidentate phosphine ligand (dppe) coordinated to Ru(II) center by bond distances of Ru–P(1) = 2.286(2) Å and Ru–P(2) = 2.268(2) Å and bite angle of 82.57°. The Ru-bonded Cp are essentially planar with C–C bond length, giving a mean value of 1.403 Å and Ru-Cp_{Cent} bond distance of 1.865 Å. There are two molecules of **1** in each unit cell that connected each other by C–H···π interaction [$C(9)–H(9)^{i} \ldots C_{cent}(C21–C26)^{ii}$] = 2.857 Å (i = 1 − x, −1/2 + y, 1 − z and ii = x, y, z). Furthermore, a weak hydrogen bond exists between the C–H bond of phenyl group of phosphine ligand and chloride ions of the next molecule [$C(27)–H(27)^{iii} \ldots Cl(1)^{ii}$] = 2.935 Å

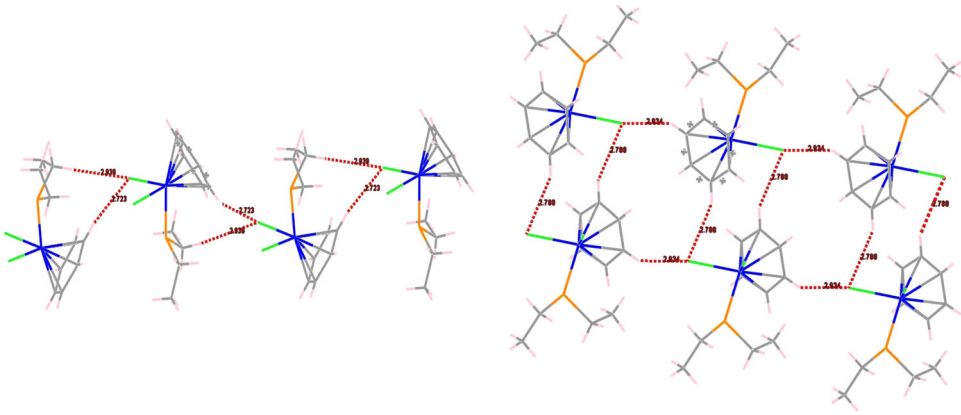


Figure 2. View of C–H … Cl hydrogen bonding (red line) in $[(C_6H_6)RuCl_2(PEt_2H)]$.

(iii = 1 + x, y, 1 + z) with angle of 133.01° that is stabilizing the structure of the complex.

$[(C_6H_6)RuCl_2(PEt_2H)]$ has four molecules in packing and it has same conformation with **1** consisting of a monodentate phosphine ligand (PEt_2H) and two chlorine atoms with bond distances of Ru–P = 2.310 Å, Ru–Cl(1) = 2.401 Å and Ru–Cl(2) = 2.416 Å, comparable with reported bond lengths in similar ruthenium complexes [38]. The benzene ring that is connected to the ruthenium center shows a disorder position which was caused by an internal rotation around the central axis of the molecule. This disordered configuration is normal for benzene ring in room temperature and upon cooling, the benzene ring becomes ordered [39]. Distance from ^{6}-coordinated benzene centroid and Ru atom is 1.673 Å. The C–H···Cl interactions play an important role in assembly of this complex and contribute to stabilize the crystal structure. One of the chlorine atoms of each molecule (Cl_1) interacted by two C–H bonds, $[C(12)–H(12)^{iv} \ldots Cl(1)^{ii}] = 2.723$ Å and $[C(3)–H(3A)^{v} \ldots Cl(1)^{ii}] = 2.932$ Å of next molecule. Another chlorine atom is connected by C–H bond of benzene ring in two separate molecules, $[C(1)–H(1)^{vi} \ldots Cl(2)^{ii}] = 2.788$ Å and $[C(13)–H(13)^{vi} \ldots Cl(2)^{ii}] = 2.934$ Å; these two interactions are shown in Figure 2 (iv = 1 − x, 1 − y, 1 − z, v = −1 + x, y, z and vi = −1/2 + x, 1/2 − y, −1/2 + z).

3.2. Catalytic studies

Herein, secondary amines were prepared with good chemo-selectivity from reaction of aliphatic alcohols with urea in the presence of catalytic amounts of ruthenium complexes. In this context, a series of ruthenium phosphine complexes have been synthesized and tested in the reaction of hexylalcohol and urea in ethylene glycol dimethyl ether as solvent. As shown in Table 3, octahedral complexes (entries 7–12) showed less reactivity compared to four-coordinate complexes. It shows the importance of free coordination sites on metal centers to increase activity of complexes [40]. This is confirmed by the least activity of octahedral diphosphine complexes in these series.

Complex **1** showed higher catalytic activity than **2** (entries 3 and 4 in Table 3). It was proposed that catalytic dehydrogenation of alcohols can be facilitated by an

Table 3. Amination of hexyl alcohol with urea in the presence of different ruthenium catalysts.

			Selectivity		
Entry	Complex	Conversion	1°Amine	2°Amine	3°Amine
1	No catalyst	–	–	–	–
2	$RuCl_3{\cdot}xH_2O$	61	2	94	4
3	[(Cp)RuCl(dppe)]	99	9	90	1
4	$[(C_6H_6)RuCl_2(PHEt_2)]$	95	10	90	
5	$[Ru(cymene)Cl_2]_2$	91	9	90	1
6	$[(Cp)RuCl(PPh_3)_2]$	88	12	86	2
7	$[RuH_2(CO)(PPh_3)_3]$	83	19	81	–
8	$[RuCl(OAc)(PPh_3)_3]$	79	12	87	1
9	$[RuCl_2(dppe)_2]$	65	24	61	15
10	$[RuCl_2(dppm)_2]$	60	12	76	12
11	$[RuCl_2(dppp)_2]$	62	7	82	11
12	$[RuCl_2(dppb)_2]$	59	6	85	9
13	[(Cp)RuCl(dppe)][a]	96	15	83	2

Reaction conditions: 2.5 mmol hexyl alcohol, 2.5 mmol urea, 3 mol% catalyst, 0.07 mmol (dppp) supporting ligand, 1.5 mL diglyme, 12 h and 160 °C.
[a]6 mol% of catalyst was used.

electron-rich metal center. Therefore, bidentate phosphine ligand has been found to have a stronger effect, perhaps due to the higher basicity and stronger coordination ability compared to mono phosphine ligand, PEt_2H. Among the ruthenium complexes with diphosphine ligands, the selectivity was likely controlled by the strict environment around the metal center (entries 9–12 in Table 3). *cis*-$[RuCl_2(dppp)_2]$ showed the best activity in this group of catalysts. The selectivity of the complexes depends on the ligand's size, as smaller diphosphines (dppm and dppe) showed higher selectivity for primary amines while increasing the bridge length for bulky diphosphine (dppp and dppb) leads to higher selectivity for secondary amines. From the experimental results we chose 3 mol% of catalyst as the optimum value for proper conversion, while, with increasing the amount of catalyst, no positive effect on the reaction conversion was obtained (entry 13).

In this reaction, only with careful adjustment of reaction parameters, such as the relative proportion of the reactants, reaction temperature and the use of proper additives one can tune conditions, so that the desired product becomes predominant. Encouraged by the results obtained by [(Cp)RuCl(dppe)] (**1**), this complex was used for further investigation to find the effect of different parameters on reaction conversion and selectivity (Table 4). In this regard, the effect of reaction temperature was examined from 120 to 170 °C. Excellent results were obtained when the reactions were performed at 160 °C, during which a total conversion of over 90% was obtained under our mentioned experimental conditions. A complete hydrolysis of urea did not occur during the reactions from 120 to 130 °C, so after 12 h of reaction at 130 °C, unreacted urea remained in the autoclave. As shown in Table 4, for reaction of aliphatic alcohols even a higher temperature is required. The reaction was considerably accelerated by increasing temperature and for reaction of hexylalcohol with urea at 160 °C proper yield for secondary amine was obtained.

Effect of alcohol to urea mole ratio on n-alkylation reaction is summarized in Table 5. The hydrolysis of urea leads to formation of two moles of ammonia and one mole of carbon dioxide, resulting in a rise in alkalinity of the mixture as the reaction proceeds. Alkali conditions can expedite dehydrogenation of alcohols and formation

Table 4. Effect of temperature on amination of aliphatic and aromatic alcohols with urea.

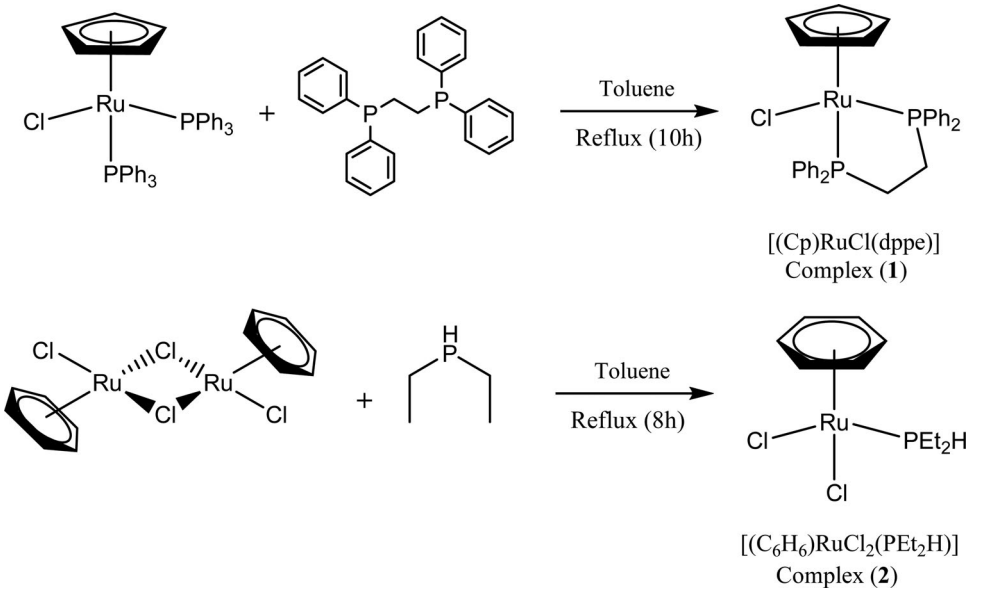
				Selectivity		
Entry	Alcohol	Temperature (°C)	Conversion	1°Amine	2°Amine	3°Amine
1	Benzylalcohol	120	20	89	11	–
2	Benzylalcohol	130	28	84	16	
3	Benzylalcohol	140	50	60	40	–
4	Benzylalcohol	150	86	59	39	–
5	Benzylalcohol	155	97	54	46	–
6	Benzylalcohol	160	100	51	44	5
7	Benzylalcohol	165	100	48	45	7
8	Benzylalcohol	170	100	44	44	12
9	Hexyl alcohol	150	55	40	60	–
10	Hexyl alcohol	155	85	25	74	1
11	Hexyl alcohol	160	94	21	78	1
12	Hexyl alcohol	170	96	9	83	8

Reaction conditions: 2.5 mmol alcohol, 2.5 mmol urea, 3 mol% complex 1, 0.07 mmol (dppp) supporting ligand, 1.5 mL solvent, 12 h. Yields were determined by GC.

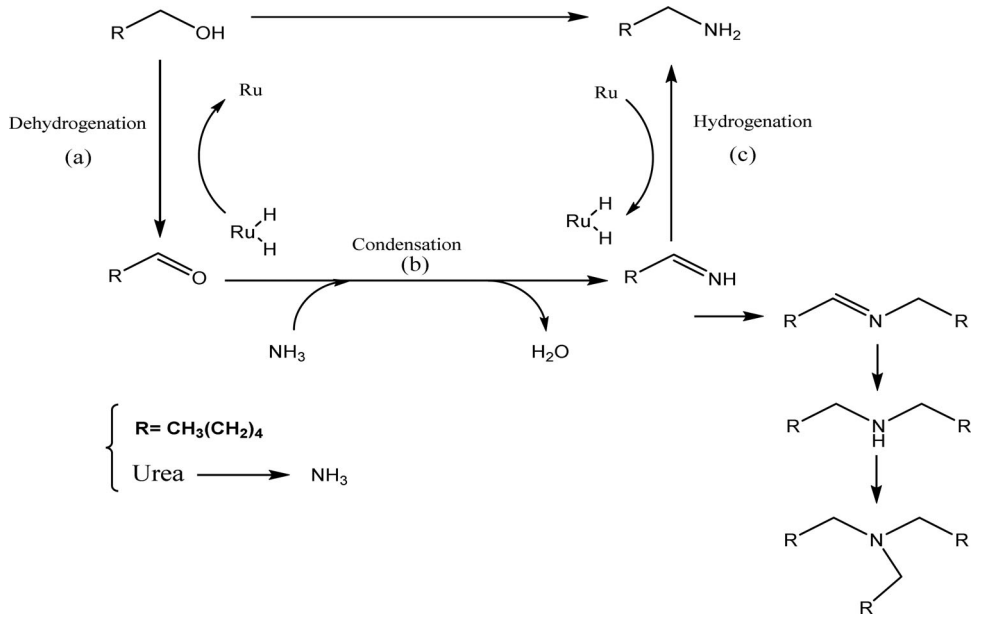
Table 5. Effect of alcohol to urea mole ratio on amination of alcohol with urea.

				Selectivity		
Entry	Substrate	Ratio alcohol/urea	Conversion	1°Amine	2°Amine	3°Amine
1	Benzylalcohol	4	88	1	77	22
2	Benzylalcohol	2	97	2	81	17
3	Benzylalcohol	1	100	8	81	11
4	Hexyl alcohol	4	81	1	83	16
5	Hexyl alcohol	2	93	3	95	2
6	Hexyl alcohol	1	98	10	88	2
7	2-Ethylhexanol	4	73	48	52	–
8	2-Ethylhexanol	2	77	55	45	–
9	2-Ethylhexanol	1	88	61	39	–

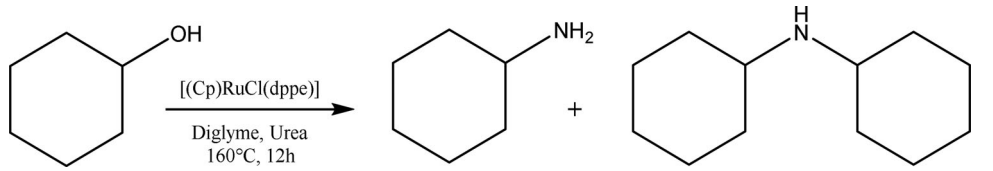
Reaction conditions: 2.5 mmol alcohol, 3 mol% complex 1, 0.07 mmol (dppp) ligand, 1.5 mL diglyme, 12 h and 160 °C. Yields were determined by GC.



Scheme 1. Synthesis route for preparation of ruthenium complexes [36].



Scheme 2. Hydrogen-borrowing mechanism of amination reaction of aliphatic and aromatic alcohols. (a) dehydrogenation, (b) condensation, (c) hydrogenation.



Scheme 3. Direct synthesis of cyclohexylamine and dicyclohexylamine from cyclohexanol and urea catalyzed by **1** [37].

of related aldehydes [41]. On the basis of reaction mechanism, the direct synthesis of amine by alcohol proceeds through three steps (Scheme 2). In the first step (a), the dehydrogenation of the alcohol initially gives the corresponding carbonyl compound, the reaction of which with the NH_3 produced by urea hydrolysis leads to the formation of an imine intermediate (b) and then subsequent hydrogen transfer to the resultant imine yields the corresponding primary amine (c). In the overall reaction, the second and third N-alkylations proceed by similar processes and lead to secondary and tertiary amines [20, 27].

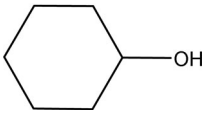
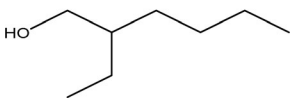
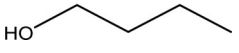
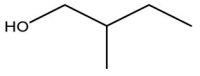
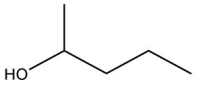
After several experiments we found that 2 moles of alcohol per mole of urea is the optimum amount for having the best reactivity and we reached 93% conversion with 95% selectivity toward secondary amines. By changing this ratio to 4, conversion was 81% but when stoichiometric amounts of urea and alcohol were used 98% conversion with lower selectivity for secondary amine was obtained. The same trends were seen for other aliphatic alcohols. In addition, when a higher mole ratio of urea respect to alcohol was used a large amount of unknown by-products were produced. The alcohol to urea mole ratio of 2 was chosen as the optimum ratio afterwards.

Table 6. Effect of supporting ligand on amination of alcohols with urea.

			Selectivity		
Entry	Supporting ligand	Conversion	1°Amine	2°Amine	3°Amine
1	No ligand	30	50	50	–
2	Xantphos	98	24	76	–
3	PPh_3	73	10	79	11
4	dppe	50	20	70	10
5	dppm	82	12	81	6
6	dppp	98	8	91	1
7	dppb	98	26	73	–
8	dpppe	93	34	66	–

Reaction conditions: 2.5 mmol 1-hexylalcohol, 0.12 mmol urea, 3 mol% complex **1**, 0.07 mmol phosphine supporting ligand, 1.5 mL diglyme, 12 h and 160 °C.

Table 7. Amination of primary and secondary alcohols with urea.

			Selectivity		
Entry	Substrate	Conversion	1°Amine	2°Amine	3°Amine
1	Octanol 	98	12	88	–
2	Cyclohexanol 	90	40	60	–
3	2-Ethylhexanol 	92	62	38	–
4	Butanol 	87	14	75	1
5	2-methyl-butanol 	90	52	48	–
6	Isoamylalcohol 	89	17	83	–

Reaction conditions: 2.5 mmol alcohol, 2.5 mmol urea, 3 mol% complex **1**, 0.07 mmol (dppp) ligand, 1.5 mL solvent, 12 h and 160 °C.

A range of phosphine ligands have been used to investigate the importance of supporting ligands in the course of the reaction and the results are shown in Table 6. Supporting ligand has a very important effect on this reaction and in the absence of free supporting ligand very low conversion will be obtained (entry 1, Table 6). For having high conversion, using an excess amount of free ligand is crucial. Phosphine ligands may displace the complex aldehyde to facilitate its reaction in solution with amine or it may accelerate the catalytic hydrogenation of imine [27]. Under experimental reaction conditions a common phosphine ligand, such as triphenylphosphine, showed low conversion. Enhancement of the product yield with suitable chemo-selectivity was observed using diphenylphosphinopropane (dppp), while the medium yield was the only outcome of using structurally similar diphenylphosphinomethane (dppm) and diphenylphosphinoethane (dppe). Moreover, by bulky diphenylphosphinobutane (dppb), diphenylphosphinopentane (dpppe) and xantphos satisfying results were obtained. Under these conditions primary amines did not proceed to secondary amines so the selectivity has been decreased. This ruthenium catalytic system was tested for preparation of amines from other alcohols under the optimum conditions. Good yields were obtained for the amination of alcohols which can be seen in Table 7. For sterically hindered 2-ethylhexanol and 2-methylbutanol, the percentage of primary amine increased in comparison with octanol and butanol. These results show that steric hindrance has affected selectivity of amines and led to decrease in selectivity toward secondary amines.

Also we tested the applicability of this method for the amination of a secondary alcohol, cyclohexanol (Scheme 3). Due to difficulty in dehydrogenation step as well as the hydrogenation of the iminium or enamine intermediates, secondary alcohols are more challenging in amination reaction using hydrogen borrowing strategy. With the current catalytic system cyclohexanol results in a mixture of primary and secondary amines with 90% conversion.

4. Conclusion

A simple and environmentally benign homogeneous catalytic route introduced for the direct synthesis of amines by reaction of alcohols with inexpensive and readily available urea as a convenient nitrogen source. [CpRuCl(dppe)] was selected as an active catalyst and it showed proper activity and selectivity for secondary amine under the experimental reaction condition.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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