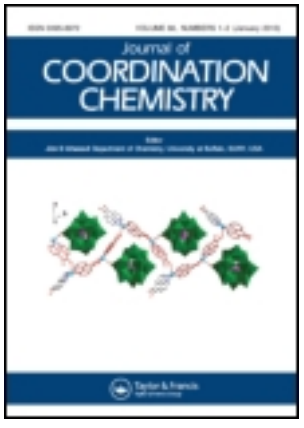

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N-alkylation of amines by homogeneous ruthenium complexes in the presence of free diphosphines

Bahareh Tamaddoni Jahromi[a] & Ali Nemati Kharat[a]

[a] School of Chemistry, University College of Science, University of Tehran, Tehran, Iran

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N-alkylation of amines by homogeneous ruthenium complexes in the presence of free diphosphines

BAHAREH TAMADDONI JAHROMI and ALI NEMATI KHARAT*

School of Chemistry, University College of Science, University of Tehran, Tehran, Iran

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Chemoselective N-alkylation of amines by ruthenium complexes in the presence of free diphosphine ligands under mild conditions is described. Octyl amine and aniline were chosen as aliphatic and aromatic amines to investigate the effect of different phosphines, reaction times, and temperature on conversion, as well as selectivity towards related secondary and tertiary amines. After optimization of the reaction conditions, this catalytic system was used for N-alkylation of other amines and has shown moderate to very good yields. The reaction products were monitored by GC–MS. The crystal structure of $[Ru(NO_3)_2CO(PPh_3)_2]$ with a monodentate and a bidentate nitrate was determined by X-ray crystallographic analysis.

Keywords: N-alkylation; Homogeneous catalyst; Ruthenium complex; Diphosphines

1. Introduction

Syntheses of amines have received attention in bulk and fine chemical industries [1]. Due to their interesting physiological activities, amines are extremely important pharmacophores in numerous biologically active compounds and have been touted in the area of drug discovery [2]. Aromatic secondary amines play a key role in petrochemical, pharmaceutical, agrochemical, and food additives [3]. Despite widespread interest, methods of amine preparation are often problematic because of harsh reaction conditions, poor yields, and low chemical selectivities [4]. Traditionally, the alkylation of amines is performed using conventional alkylating agents, such as alkyl halides. This route has serious selectivity problems because of multiple alkylations. Catalytic methodologies, such as reductive amination, hydroamination, and hydroaminomethylation of olefins or alkynes, have been developed for the synthesis of amines [5–8]. Buchwald and co-workers have made considerable contributions towards the development of reliable and practical catalysts for the formation of aromatic carbon nitrogen bonds by cross-coupling of amines and aryl halides [9]. The disadvantages of these reactions are high temperatures and long reaction times required to obtain optimum yields. Therefore, the development of a selective N-alkylation method that is cost effective, salt-free, and environmentally acceptable is of considerable interest. There is ongoing interest for improving previous methods and developing new efficient synthetic routes [10]. N-alkylation of amines with alcohols [11] in place of alkyl halides, tosylate, mesylate, or triflate has attracted interest and is well documented [10, 12]; known since the

*Corresponding author. Email: alnema@khayam.ut.ac.ir

beginning of the twentieth century, yet the reaction conditions are difficult for industrial applications. Therefore this method was explored using different additives. Alcohol condensation with aromatic amines in the vapor phase using various catalysts has enjoyed synthetic utility in the introduction of an alkyl functionality on nitrogen. Numerous catalysts have been explored in the reaction of an aromatic primary amine with an alcohol to form a product containing an N-alkyl-substituted amine allowing a wide variety of environmentally safe heterogeneous catalysts to be developed [13, 14]. Alcohols have been condensed with amines using transition metal catalysts such as nickel [14, 15], rhodium [16], or ruthenium [17]. All of these heterogeneous catalysts suffer from low selectivity and harsh conditions. The first example of a homogenous catalyst in this field was published by Grigg and Watanabe [18], followed by reports from the Beller group using bulky phosphines and ruthenium carbonyl complexes [19–21]. Hartwig investigated the addition of anilines to pseudo-halides and aryl triflates catalyzed by a soluble palladium complex and diphenylphosphino ferrocene [22]. The advantage of this procedure in comparison with the traditional methods is the high selectivity under mild conditions.

The amination of alcohols involves three well-known steps; the oxidation of an alcohol into a carbonyl with a transition metal catalyst, imine formation between an amine and a carbonyl compound, and the reduction of imine to amine. These systems have disadvantages, for example, the recovery and reuse of expensive catalysts and the need of co-catalysts, such as bases and stabilizing ligands. Therefore, the search for cheaper catalysts with the same performance is necessary for industrial application. Ruthenium-based homogeneous catalytic systems are relatively cheaper than other transition metal catalysts, such as iridium and rhodium and are mostly commercially available.

In this research, we investigate N-alkylation of several aromatic and aliphatic amines with benzyl alcohol by ruthenium complexes under relatively mild conditions. Under our experimental conditions, ruthenium catalysts have no activity in the absence of phosphine ligands. A number of diphosphine ligands were added to the reaction mixture and their activities and selectivities were compared. The reactions were run in different solvents, temperatures, and reaction times to find optimum conditions.

2. Experimental

2.1. *Materials and instrumentation*

All chemicals and reagents were purchased from Aldrich and Strem chemical companies and used without purification. The solvents were of analytical grade, and purified prior to use based on standard methods. Amines were distilled under argon and stored in tightly closed containers. Reactions were carried out under inert atmosphere using standard Schlenk techniques. Melting points are uncorrected and were obtained with the Electrothermal 9200 melting point apparatus. For monitoring of reaction products and their identity, a gas chromatograph, Agilent Technologies 7890A Instrument (equipped with a HP-1 capillary column, a FID detector, and a mass spectroscope model 5975C with a triple-axis detector), was used. Dodecane was used as the internal standard.

2.2. *Synthesis of complexes*

Xantphos derivatives were prepared according to previously published methods [23]. $[Ru(p\text{-cymene})Cl_2]_2$, $[RuCl(PPh_3)_2Cp]$, $[RuHCl(CO)(PPh_3)_3]$, $[RuH_2CO(PPh_3)_3]$, and

[Ru_3CO_{12}] were prepared according to literature methods [24–26]. For preparation of crystals of [$Ru(NO_3)_2CO(PPh_3)_2$] and [$Ru(NO_3)_2(CO)_2(PPh_3)_2$], a slightly modified method was used [27]. Typically 0.1 g [$RuH_2CO(PPh_3)_2$] was refluxed in 3 M nitric acid (25 mL) for 3 h. The resultant viscous oil was separated by decantation and dried over sodium sulfate. The product was filtered off and dissolved in dichloromethane/methanol. After cooling to 10 °C, yellow cubic crystals of $Ru(NO_3)_2CO(PPh_3)_2$ appeared (yield 60%). mp: 269–271 °C. Elemental Anal. Calcd for $C_{37}H_{30}N_2O_7P_2Ru$: C, 57.12; H, 3.88; N, 3.60. Found: C, 57.26; H, 3.91; N, 3.68. For the preparation of [$Ru(NO_3)_2(CO)_2(PPh_3)_2$], carbon monoxide was bubbled through a suspension of 0.2 g [$Ru(NO_3)_2CO(PPh_3)_2$] in boiling ethanol (30 mL) for 2 h. After cooling the mixture, white solids were separated and washed with ethanol (yield 92%). mp: 180–183 °C. Elemental Anal. Calcd for $C_{38}H_{30}N_2O_8P_2Ru$: C, 56.65; H, 3.75; N, 3.48; found: C, 56.57; H, 3.78; N, 3.37.

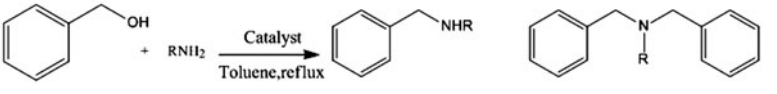
2.3. *N-alkylation reaction*

Ruthenium complex (0.015 mM), diphosphine ligand (0.07 mM), potassium carbonate (0.03 mM), and activated molecular sieves 3Å (0.1 g) were added to the reaction flask. The mixture was exposed to nitrogen for 10 min. Amine (1.0 mM), benzyl alcohol (1.0 mM), and dry toluene as solvent (1.0 mL) were added and refluxed for 12 h. After filtration, the reaction mixture was extracted three times with 5% hydrochloric acid solution, then the pH of the combined aqueous phase was adjusted to nine by the addition of dilute sodium hydroxide solution. The aqueous phase was extracted with dichloromethane and dried over $MgSO_4$ prior to the injection to GC.

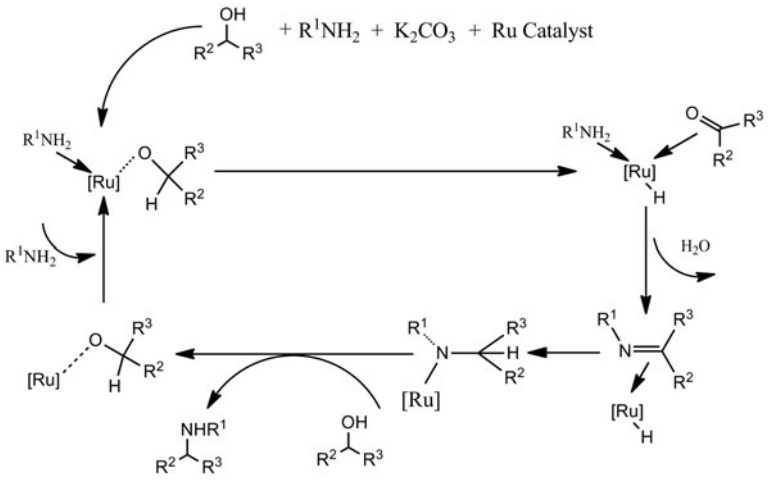
3. Results and discussion

The N-alkylation of amines by alcohols is a thermodynamically favored process. This reaction has synthetic importance in the preparation of secondary and tertiary amines. Herein, we report the N-alkylation of several aliphatic and aromatic amines with benzyl alcohol in the presence of different ruthenium catalysts (scheme 1). Secondary amines, because of their higher nucleophilicity, are generally more reactive than primary amines, such that further reaction favored the formation of tertiary amines. Our primary goal was to find suitable conditions for chemoselective synthesis of amines.

The mechanism of N-alkylation of amines with alcohols in the presence of transition metal catalysts are shown in scheme 2. This reaction proceeds stepwise, whereby the ruthenium catalyst dehydrogenates the alcohol to form an aldehyde that is readily attacked by the amine, then transformed initially into the imine, where concentration remains low and almost constant throughout the reaction [28]. A successive hydrogenation converts the imine into the N-alkyl derivative. This third step uses the hydrogen which was removed



Scheme 1. N-alkylation of amines with benzyl alcohol.



Scheme 2. Mechanism of ruthenium catalyzed N-alkylation of amines with alcohols.

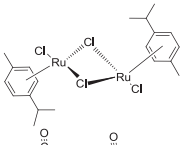
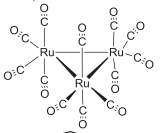
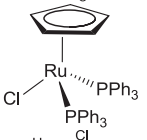
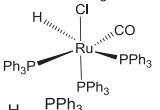
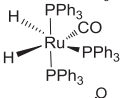
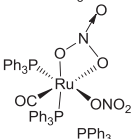
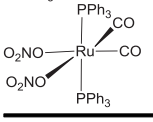
from the alcohol in the first step. Thus, an overall redox reaction is catalyzed with a series of steps involving both oxidation and reduction.

In the above mechanism, water was formed as the reaction proceeded, which can lead to increased hydrolysis of the imine to yield the ketone, which can also be hydrogenated by the catalyst. Thus, in most cases, for the removal of water from the reaction medium molecular sieves were used, having a beneficial effect on these reactions. Another common protocol includes the presence of an inorganic base or ammonia to affect the aforementioned transformation. The most conventional conditions utilize an alkali metal carbonate in a polar aprotic solvent at room temperature or under heating, depending on the nature of the starting materials. As mentioned in the published literature [29], this additive has a crucial effect on both conversion and selectivity. Some work claimed that it can render formation of tertiary amines [30] in the course of the reaction. According to scheme 2, addition of an alkali can expedite dehydrogenation of alcohols and formation of related aldehydes. Another effect of alkali addition should be increasing nucleophilic power of the amines.

In table 1, activities of various ruthenium complexes in N-alkylation of amines are shown. Catalyst loading was 3 M% based on the ruthenium complex. The combination of diphenyl-phosphinopropane (dppp) with different ruthenium complexes under mild conditions was chosen as the model reaction to find the active ruthenium complexes.

As shown in table 1, among the synthesized complexes, $[(Ru(Cymene)Cl_2)_2]$, $[Ru_3CO_{12}]$ and $[RuCl(PPh_3)_2Cp]$ show good activity and $[(Ru(p\text{-cymene})Cl_2)_2]$ appeared to be the most effective catalyst. Under the experimental conditions of this study, $[RuHClCO(PPh_3)_3]$ and $[RuH_2CO(PPh_3)_3]$ show less reactivity. It was proposed that a free coordination site on ruthenium is necessary for activation in this type of reaction. In these saturated metal hydride complexes, an energy consuming preliminary ligand dissociation is the reason for low or even no reactivity. Normally, 16-electron complexes are active in dehydrogenation and the 18-electron complexes are active in hydrogenation reactions [31]. Unexpectedly, $[Ru(NO_3)_2CO(PPh_3)_2]$ showed better activity than other 18-electron complexes studied in this paper.

Table 1. Conversions of ruthenium complexes in N-alkylation of amines.

Catalyst	n-Butylamine	Hexylamine	Octylamine	Cyclohexylamine	Aniline
	96	93	94	89	89
	80	77	74	80	82
	63	56	50	61	51
	34	28	25	15	10
	29	30	25	12	14
	77	68	75	62	65
	41	38	38	31	30

Notes: Reaction condition: 1 mM amine, 1 mM benzyl alcohol, 3 M% ruthenium catalyst, 0.07 mM dppp, 0.03 mM base, 1 mL toluene, 110 °C, 12 h. Yields were determined by GC.

X-ray crystallography of $[Ru(NO_3)_2CO(PPh_3)_2]$ confirmed the six-coordinate geometry with one monodentate and one bidentate nitrate in the complex. Switching from a bidentate to a monodentate nitrate should provide a vacant site for the coordination of alcohol or amine. Crystallographic data and selected bond lengths and angles are listed in tables 2 and 3, respectively. $[Ru(NO_3)_2CO(PPh_3)_2]$ crystallizes as yellow cubes in the monoclinic space group C2/c with 8 molecules in the unit cell (figure 1).

The ruthenium–oxygen bond distance is 2.133(3) Å for monodentate and 2.149(3) and 2.166(2) Å for bidentate nitrate, comparable with reported bond lengths for a six-coordinate ruthenium complex [32–34]. Another reason for unusual reactivity is the high tendency of $[Ru(NO_3)_2CO(PPh_3)_2]$ for alcohol dehydrogenation [35]. This reaction, which is accelerated in the presence of a base, proceeds by a β-elimination mechanism, and is accompanied by the formation of an aldehyde and a metal hydride, $[RuH(NO_3)(CO)(PPh_3)_2]$, by a nitrate dissociation; the steps are shown in the catalytic scheme 2. The unit cell-packing diagram of the complex is presented in figure 2.

Some weak hydrogen bonds exist in the structure, stabilizing the packing of the complex. One of these hydrogen bonds exists between the C–H bond of phenyl and oxygen of nitrate of the next molecule (C(4)–H(4)···O(7) = 2.30 with an angle of 160.2 and C(29)–H(29)···O(2)

Table 2. Crystallographic and structure refinement data of $Ru(NO_3)_2CO(PPh_3)_2$.

Formula	$C_{37}H_{30}N_2O_7P_2Ru$
Formula weight	777.64
Crystal system	Monoclinic
Space group	C 2/c
a/Å	19.111(4)
b/Å	10.741(2)
c/Å	34.370(7)
α/°	90
β/°	100.26
γ/°	90
Volume/Å^3	6942(2)
Z	8
Density (Calcd)/gm	1.488
θ Ranges for data collection	2.21–29.15°
F (0 0 0)	3168
Absorption coefficient/mm^{-1}	0.596
Index ranges	$-26 \le h \le 26$, $-12 \le k \le 14$, $-47 \le l \le 47$
Data collected	26864
Unique data (R_{int})	9259 (0.0475)
Parameters, restraints	412, 0
Final R_1, wR_2[a] (obs. data)	0.0611, 0.1257
Final R_1, wR_2[a] (all data)	0.0807, 0.1335
Goodness of fit on F^2(S)	1.064
Largest diff. peak and hole/eÅ^3	1.622, −1.188

Note:[a]$R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$; $wR_2 = [\Sigma(w(F_0^2-F_c^2)^2)/\Sigma w(F_0^2)^2]^{1/2}$.

Table 3. Selected bond distances (Å) and angles (°) for $[Ru(NO_3)_2(CO)(PPh_3)_2]$.

Ru(1)–C(37)	1.838(4)
Ru(1)–O(5)	2.133(3)
Ru(1)–O(2)	2.149(3)
Ru(1)–O(3)	2.166(2)
Ru(1)–P(1)	2.312(1)
C(37)–Ru(1)–O(5)	100.42
O(5)–Ru(1)–O(2)	79.98
C(37)–Ru(1)–O(3)	59.84
O(2)–Ru(1)–P(1)	160.95

with an angle of 170.6). The other hydrogen bond belongs to C–H$\cdots\pi$ interaction of the phenyl groups (figure 3).

In this type of reaction, using alkylating agent in a limited amount is not sufficient for selective synthesis of a given product and only with careful adjustment of reaction parameters, such as the relative proportions of the reactants, reaction temperature, time, and the use of proper additives [36, 37], can one tune conditions, so that the desired product becomes predominant. Other constraints such as amine basicity, steric demands, and relative solubilities in the reaction media [38, 39] need to be taken into account if product yields are of importance.

Using an excess of free ligand is crucial for high conversion. Previous researchers suggested that phosphine may displace the complexed aldehyde to facilitate its reaction in solution with amine [40] or that it may accelerate the catalytic hydrogenation of imine to

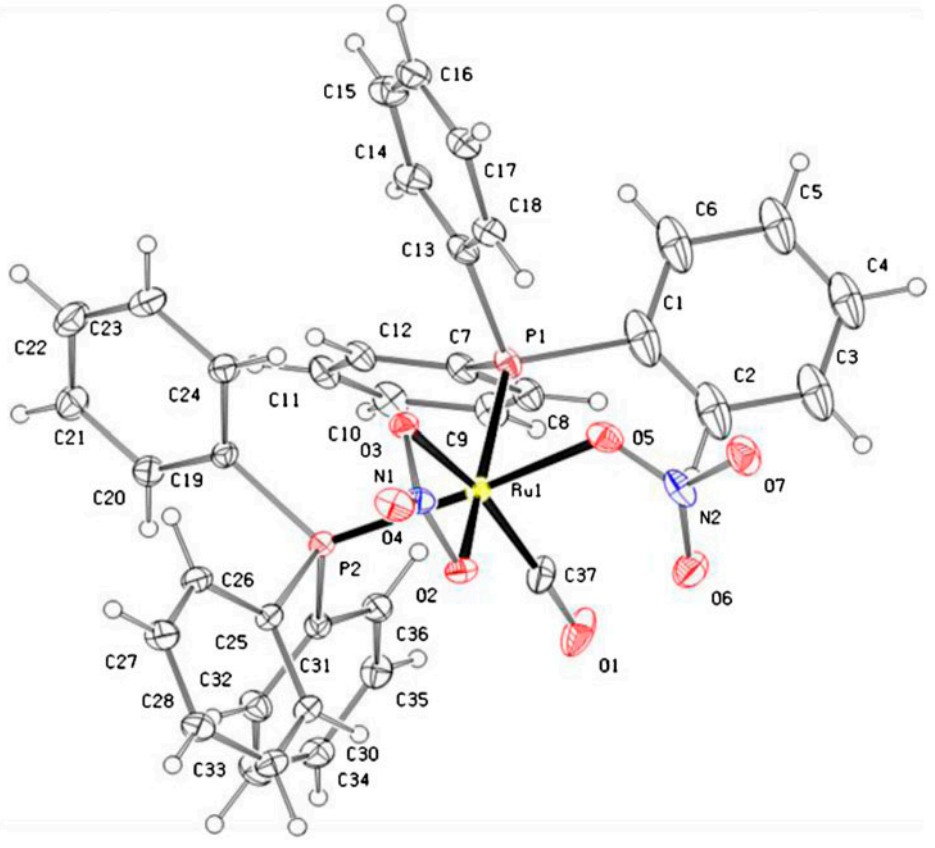


Figure 1. ORTEP of $Ru(NO_3)_2CO(PPh_3)_2$ with atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level at 298 °K.

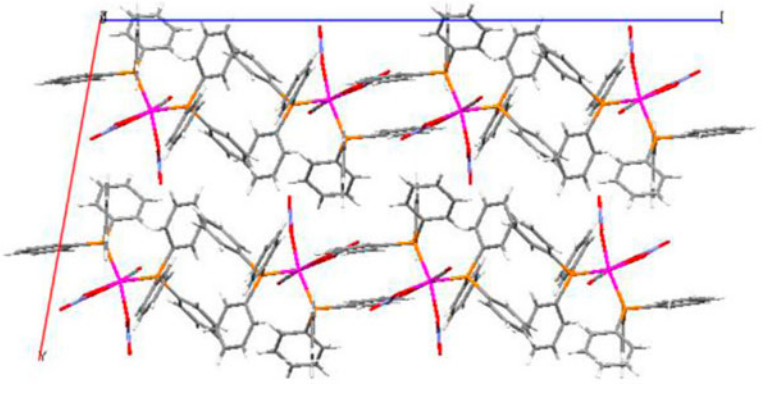


Figure 2. Packing view of $Ru(NO_3)_2CO(PPh_3)_2$.

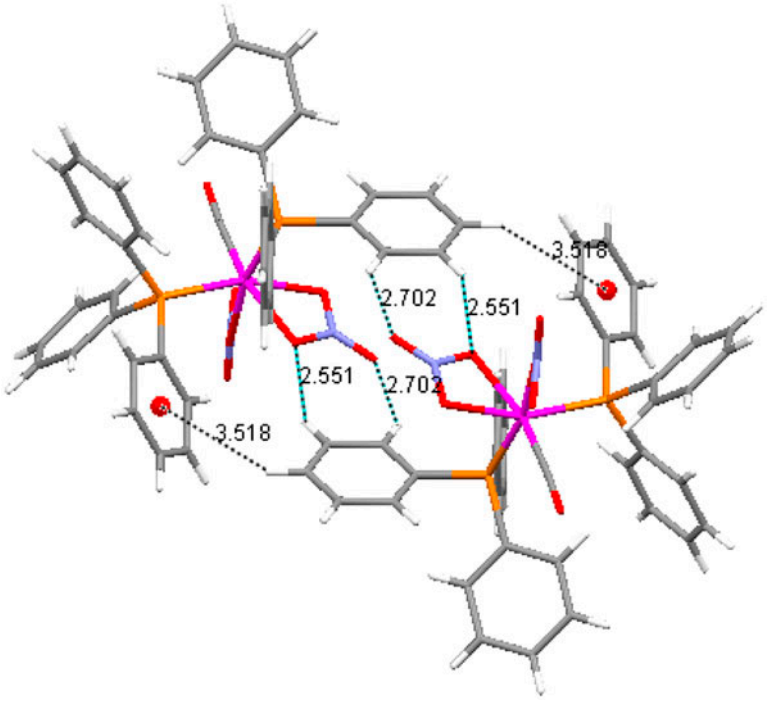


Figure 3. View of C–H···O hydrogen bonding (blue dashed line) and C–H···π interactions (black dashed line) in the packing (see http://dx.doi.org/10.1080/00958972.2013.844340 for color version).

tertiary amine. To further investigate the importance of ligands in the course of this reaction, a series of diphosphine ligands, such as xantphos and their calcogenides, xantphos oxide, xantphos sulfide, and xantphos selenide, diphenylphosphinomethane (dppm), diphenylphosphinoethane (dppe), diphenylphosphinopropane (dppp), diphenylphosphinobutane (dppb), and diphenylphosphinopentane (dpppe) were tested in the N-alkylation reaction of benzyl alcohol. Octyl amine and aniline were chosen as probes of aliphatic and aromatic amines to investigate the effect of ligands. In the absence of any additional ligand, only low conversion of the starting material after 12 h at refluxing toluene was obtained for all catalysts. A high yield of the product with good chemoselectivity was obtained using diphenylphosphinopropane (dppp), while the structurally similar dppm, dppe, and dpppe provided only poor yields. As shown in table 4 comparison of different xantphos derivatives show that replacing the soft donor P in xantphos with hard O in xantphos oxide, conversions increased significantly. Xantphos oxide showed better conversion than other calcogenides. In the reaction with xantphos derivatives, better selectivity is observed toward secondary amines in the reaction with aniline. Because of higher nucleophilicity, secondary amines are generally more reactive than primary amines, so further reaction favored the formation of tertiary amines. Under our experimental conditions, using bulky xantphos derivatives gave higher selectivity for secondary amines.

Some authors [41] have pointed out that the presence of a chloride is a prerequisite for catalytic activity in N-alkylation reactions. However, this does not apply to our catalytic systems, because we observe good conversion using catalysts containing no chloride in

Table 4. Effect of different ligands on conversion and selectivity of ruthenium complexes in N-alkylation of amines.

		Octyl amine			Aniline		
Entry	Ligand	Conv. %	°2 Amine	°3 Amine	Conv. %	°2 Amine	°3 Amine*
1	No ligand	8	–	–	5	–	
2	Xantphos	75	15	79	73	43	55
3	Xantphos=O	88	18	81	84	55	40
4	Xantphos=S	80	24	73	80	74	23
5	Xantphos=Se	77	23	74	75	86	10
6	dppm	75	28	70	69	39	61
7	dppe	83	30	69	78	45	50
8	dppp	94	23	74	89	50	50
9	dppb	83	27	72	74	43	55
10	dpppe	79	24	74	70	39	61

Notes: Reaction condition: 1 mM amine, 1 mM benzyl alcohol, 3 M% $[Ru(cymene)Cl_2]_2$, 0.07 mM diphosphine ligand, 0.03 mM K_2CO_3, 1 mL toluene, 110 °C, 12 h.
*Besides secondary and tertiary amines, small amounts of unknown heavy by-products were formed.

their structure. As shown in table 5 in the alkylation of secondary amines, basicity and size of amines are important. Secondary amines such as morpholine and diethylamine gave lower yields compared to the primary amines under the same condition and required higher catalyst loading to obtain good yields. Aromatic amines showed lower activity with respect to aliphatic amines and as expected, electron-rich toluidine showed better results than chloroaniline.

In some catalytic runs, a light-brown ruthenium containing deposit was recovered from the reaction media after completion of the reaction. Infrared spectra of these residues showed a strong absorption in the $\nu(CO_{stretch})$ at 1944 cm^{-1}, pointing to the formation of ruthenium–carbonyl complexes during the reaction. Decomposition of ruthenium aldehyde intermediates has been reported to occur during the N-alkylation reactions of long-chain aliphatic amines with primary alcohols [40]. Attempts to characterize these ruthenium-containing deposits failed because of their insolubility in common solvents. Production of

Table 5. Catalytic N-alkylation of amines with benzyl alcohol.

			Selectivity	
Entry	Starting amine	Conv.%	°2 amine	°3 amine*
1	Isopropylamine	95	50	50
2	n-Butylamine	94	44	53
3	Sec-butylamine	86	28	70
4	t-Butylamine	98	25	72
5	Hexylamine	93	30	67
6	Octylamine	94	23	74
7	Cyclohexylamine	89	24	73
8	Benzylamine	92	43	55
9	Aniline	89	50	50
10	2-Chloroaniline	86	44	53
11	Toluidine	92	45	50
12	[a]Diethylamine	60	–	86
13	[a]Morpholine	81	–	82

Notes: Reaction condition: 1 mM amine, 1 mM benzyl alcohol, 3 M% $[Ru(cymene)Cl_2]_2$, 0.07 mM dppp, 0.03 mM K_2CO_3, 1 mL toluene, 110 °C, 12 h.
[a]With catalyst loading of 10 M% only dialkylated amine was produced.
*Besides secondary and tertiary amine, small amount of unknown heavy by-products were formed.

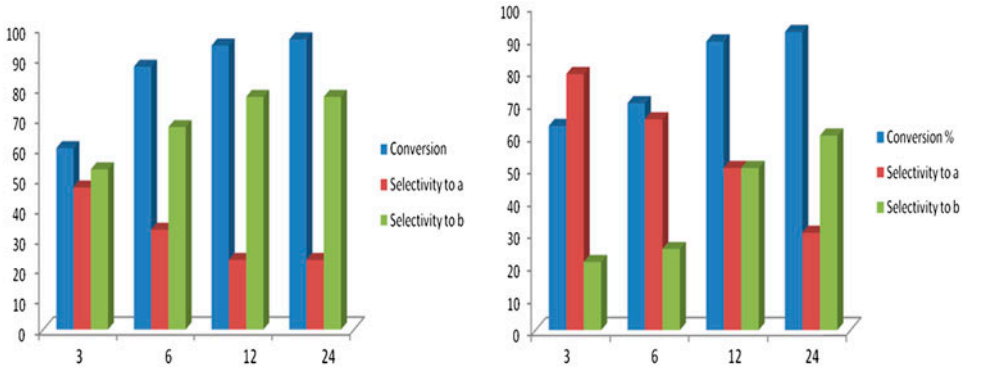


Figure 4. Effect of reaction time on alkylation of benzyl alcohol with octylamine (left) and aniline (right). Catalyst: $[Ru(cymene)Cl_2]_2$, a: secondary amine; b: tertiary amine.

such colored ruthenium-containing deposits decreased while performing the experiments at lower temperatures. Variation of solvent polarity had no significant effect on the amination reaction. The reactions were run with a molar ratio of 1:5:70:70 for catalyst:ligand:amine: alcohol in toluene as the solvent. N-alkylation of octylamine in refluxing benzene within 12 h led to 85% benzyl octylamine and 15% dibenzyl octylamine, with a total conversion of 70%. When using benzene as the solvent, the reaction stopped predominantly at the monoalkylation stage. Under these conditions, aniline was alkylated with 68% conversion and 95% selectivity to benzyl aniline. At temperatures over 140 °C by using xylene as the solvent, conversion of alcohol to alkylated amines increased over 95%, but with poor selectivity.

The influence of reaction time was examined from 4 to 24 h. Satisfying results were obtained after 12 h, during which a total conversion of over 90% was observed under our experimental conditions. As seen in figure 4, over 12 h of reaction gave no significant change in conversion; however, the selectivity dropped significantly.

After 12 h, the selectivity diminished gradually when compared to a reaction time of 6 h; using longer reaction times the amount of secondary amines decreased in favor of tertiary amines.

4. Conclusion

A number of amines with benzyl alcohol were converted into the corresponding secondary and tertiary amines with good to excellent yields. The effect of different ligands, time, and temperature were investigated in this reaction to obtain optimum conditions. This process is potentially attractive to pharmaceuticals and fine chemical industries because low loading of catalyst is needed; only H_2O is formed as the by-product and alcohols are used, which are more readily available than the potentially harmful alkyl halides or carbonyl compounds. Proceeding under transfer hydrogenation conditions, no hydrogen gas is needed for the alkylation, which allows this methodology to be a green and atom-efficient process.

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Supplementary material

CCDC number 922503 contains the supplementary crystallographic data for catalysts. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

References

[1] J.F. Hartwig. In *Handbook of Organo-palladium Chemistry for Organic Synthesis*, Wiley-Interscience, New York (2002).
[2] S.S. Insaf, D.T. Witiak. *Synthesis*, **3**, 435 (1999).
[3] M.S. Gibson. *In the Chemistry of Amino Group*, S. Patai, Interscience, New York (1968).
[4] G. Solomons, C. Fryhle. *Organic Chemistry*, Wiley, New York (2000).
[5] M. Utsunomiya, R. Kuwano, M. Kawatsura, J.F. Hartwig. *J. Am. Chem. Soc.*, **125**, 5608 (2003).
[6] J.-S. Ryu, G.Y. Li, T.J. Marks. *J. Am. Chem. Soc.*, **125**, 12584 (2003).
[7] A.M. Johns, M. Utsunomiya, C.D. Incarvito, J.F. Hartwig. *J. Am. Chem. Soc.*, **128**, 1828 (2006).
[8] T. Mizuta, S. Sakaguchi, Y. Ishii. *J. Org. Chem.*, **70**, 2195 (2005).
[9] M.C. Harris, O. Geis, S.L. Buchwald. *J. Org. Chem.*, **64**, 6019 (1999).
[10] R.N. Salvatore, C.H. Yoon, K.W. Jung. *Tetrahedron*, **57**, 7785 (2001).
[11] D.M. Roundhill. *Chem. Rev.*, **92**, 1 (1992).
[12] J.S. Bradshaw, K.E. Krakowiak, R.M. Izatt. *Tetrahedron*, **48**, 4475 (1992).
[13] K. Yamaguchi, N. Mizuno. *Angew. Chem. Int. Ed.*, **48**, 9888 (2009).
[14] C.F. Winans, H. Adkins. *J. Am. Chem. Soc.*, **54**, 306 (1932).
[15] R.G. Rice, E.J. Kohn. *J. Am. Chem. Soc.*, **77**, 4052 (1955).
[16] Y. Watanabe, Y. Tsuji, Y. Ohusugi. *Tetrahedron Lett.*, **22**, 2667 (1981).
[17] A. Baiker, J. Kijenski. *Catal. Rev. Sci. Eng.*, **27**, 653 (1985).
[18] R. Grigg, T.R.B. Mitchell, S. Sutthivaiyakit, N. Tongpenyai. *J. Chem. Soc, Chem Commun.*, 611 (1981).
[19] D. Hollmann, A. Tillack, D. Michalik, R. Jackstell, M. Beller. *Chem. Asian J.*, **2**, 403 (2007).
[20] A. Tillack, D. Hollmann, D. Michalik, M. Beller. *Tetrahedron Lett.*, **47**, 8881 (2006).
[21] A. Del Zotto, W. Baratta, M. Sandri, G. Verardo, P. Rigo. *Eur. J. Inorg. Chem.*, **524**, (2004).
[22] J. Louie, M.S. Driver, B.C. Hamann, J.F. Hartwig. *J. Org. Chem.*, **62**, 1268 (1997).
[23] B. Tamaddoni Jahromi, A. Nemati Kharat, S. Zamanian, A. Bakhoda, K. Mashayekh, S. Khazaeli. *Appl. Catal. A*, **433–434**, 188 (2012).
[24] J.P. Fackler. *Inorganic Syntheses*, Wiley Interscience Publication, New York (1982).
[25] R.J. Angelici. *Inorganic Syntheses*, Wiley Interscience Publication, New York (1990).
[26] G.W. Parshal. *Inorganic Syntheses*, Mcgraw-Hill Book Company, New York (1974).
[27] P.B. Critchlow, S.D. Robinson. *Inorg. Chem.*, **17**, 1896 (1978).
[28] M.H.S.A. Hamid, P.A. Slatford, M.J. Williams. *J. Adv. Synth. Catal.*, **349**, 1555 (2007).
[29] S.K. Srivastava, P.M.S. Chauhan, A.P. Bhaduri. *Synth. Commun.*, **29**, 2085 (1999).
[30] M.H.S.A. Hamid, M.J. Williams. *Chem. Commun.*, 725 (2007).
[31] K. Mashima, T. Nakamura, Y. Matsuo, K. Tani. *Organomet. Chem.*, **607**, 51 (2000).
[32] T. Hamaguchi, I. Ando. *Acta Cryst.*, **E67**, m1687 (2011).
[33] A. Muller, W.L. Davis. *Acta Cryst.*, **E68**, m1446 (2012).
[34] C.M. Kepert, G.B. Deacon, L. Spiccia. *Inorg. Chim. Acta*, **355**, 213 (2003).
[35] P.B. Critchlow, S.D. Robinson. *Inorg. Chem.*, **17**, 1902 (1978).
[36] R.O.C. Norman, J.M. Coxon. *Principles of Organic Synthesis*, 3rd Edn, Blackie Academic, New York (1993).
[37] H. Beyer, W. Walter. *Handbook of Organic Chemistry*, Prentice Hall, New York (1996).
[38] R.W. Alder. *Chem. Rev.*, **89**, 1215 (1989).
[39] H.C. Brown, N.R. Eldred. *J. Am. Chem. Soc.*, **71**, 445 (1949).
[40] S. Ganguly, D.M. Roundhill. *Polyhedron*, **9**, 2517 (1990).
[41] Y. Watanabe, Y. Tsuji, H. Ige, Y. Ohsugi, T. Ohta. *J. Org. Chem.*, **9**, 3359 (1984).