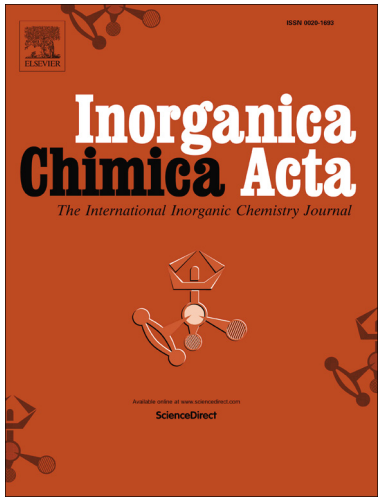

Research paper

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Ruthenium(II) complexes containing phosphino hydrazone/thiosemicarbazone ligand: An efficient catalyst for regiselective *N*-alkylation of amine via borrowing hydrogen methodology

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ABSTRACT

In the aspect of more effective ruthenium based catalyst design, three new ruthenium(II) phosphino-hydrazone/thiosemicarbazone complexes (**1-3**) have been synthesized by the reactions of *cis*-[$RuCl_2(dmso)_4$] or [$RuHCl(CO)(AsPh_3)_3$] with deprotonated 2-(2-(diphenylphosphino)benzylidene)-2-thiophenecarboxylic acid hydrazone (PNO-Thy) or 2-(2-(diphenylphosphino)benzylidene)-4-phenyl-3-thiosemicarbazone (PNS-Ph). The structures of the complexes (**2** and **3**) were established by X-ray crystallography and spectroscopic methods including elemental analysis, FT-IR and NMR (^{1}H, ^{13}C & ^{31}P). Single crystal XRD upshots of complexes (**2** and **3**) revealed a distorted octahedral geometry around the ruthenium ion with hydrazone/thiosemicarbazone acts as a monoanionic tridentate PNO/PNS donor fashion. The catalytic study of complexes **1-3** towards regioselective *N*-alkylation reactions of amines was completed, showing that all catalysts are active toward catalytic transformations. Notably, complex **3** was found to be very efficient catalysts toward *N*-alkylation of a wide range of heterocyclic amines with alcohols. This catalysis provides a clean, convenient and practical route for the direct *N*-alkyl amine synthesis.

Key words: Thiosemicarbazone, Hydrazone ligands, Ruthenium complexes, *N*-alkylation

1. Introduction

Hydrazones and thiosemicarbazones are versatile ligands of considerable attention with respect to their variable coordination behavior and promising biological [1] and catalytic properties [2]. To tune the catalytic activity or increase the activity [3], the hydrazones/thiosemicarbazones framework is functionalized by different group and studied in a number of cases [4]. Phosphino-hydrazones/thiosemicarbazones [5] occupied prominent position among the several functionalized thiosemicarbazone derivatives [6]. With the simultaneous presence of soft and hard donors, the phosphino-functionalized ligands exhibit various coordination modes: PNS-tridentate [7-9], P-S bidentate [10] and P-S bridge in binuclear compounds as well as in oligomers [11]. This makes structural studies more interesting, which are the rational base for structure-activity relationships. This variable mode of binding of phosphino-thiosemicarbazone has encouraged us to explore its coordination chemistry further although a large number of reports are available on the chemistry and biological activity of metal complexes containing thiosemicarbazonates [12-15].

The interest in coordination complexes of ruthenium stems from their versatile electron-transfer and energy-transfer properties [16]. Ruthenium offers a wide range of oxidation state and the reactivity's of the ruthenium complexes depend on the stability and inter convert ability of these oxidation states which in turn, depends on the nature of the ligands bound to the metal. Ruthenium complexes have also proved to be useful catalysts in many reactions such as oxidation, hydrogenation, carboxylation and hydroformylation [17]. Phosphine based ligands have found widespread application not only in coordination chemistry but also in industrial applications of homogeneous catalysis. Particularly, ruthenium phosphine complexes are known to possess catalytic properties which are of great value in organic synthesis [18].

The catalytic construction of C−N bonds via borrowing hydrogen methodology, have recently received much attention since nitrogen functionalities occur in various compounds of synthetic and pharmaceutical significance as well as in important biologically active molecules [19-23]. In contrast with other transition-metal-catalyzed methodologies, e.g., amination of organohalides (Buchwald-Hartwig amination) [24], reductive amination of carbonyl compounds [25], hydroamination [26] and hydroaminomethylation [27] of carbon-carbon unsaturated compounds, etc., [28] the *N*-alkylation of amines with alcohols, produced water as the sole by-

product, may serve as a relatively green and environmentally benign alternative [29]. Moreover the use of alcohols as the alkylating agent is direct and simple as the alcohols are readily available, highly stable, low in toxicity, easily stored and handled, low in cost, and relatively high in atom efficiency. While both heterogeneous and homogeneous catalysts have been known to promote the reaction [30-34], ruthenium [31-33] and iridium [34] complexes have constituted a vast majority of the homogeneous catalysts because of their relatively high catalytic performance with high product selectivity [35, 36]. Several iridium and ruthenium catalytic systems bearing phosphine ligands [37-41] have been reported to complete the *N*-alkylation of amines with alcohols by means of good yields and selectivity. Some transition-metal-free systems have been reported for the *N*-alkylation of amines with alcohols which worked under mild conditions for shorter reaction times and also provide good yields [42]. However, certain demerits of these systems such as availability, requirement of additives, poor selectivity, economy, TON etc can be overcome or improved by transition metal catalysts as alternatives.

During our ongoing exploration of highly active transition metal complex catalysts for homogeneous catalysis, we have disclosed that pyridine carboxamide, thiosemicarbazone and hydrazones with ONS, NNS, PNS and O_2N_2 functionalities [43] in Ru(II) and Cu^I complex catalyst can show a remarkable acceleration effect on the *N*-alkylation amines. Based on the above facts, the present work deals with synthesis, structures and catalytic activity of new ruthenium(II) complexes of multidentate phosphino-hydrazone/thiosemicarbazones. The new complexes have been characterized by elemental analysis, spectroscopic and X-ray crystallography studies. In addition, the complexes have also been subjected to catalytic activity.

2. Experimental

2.1 Materials and methods

All reagents were purchased from Aldrich as high-purity products and generally used as received; all solvents were used as received as technical-grade solvents. Unless otherwise noted, all reactions were performed under an atmosphere of air. Thin-layer chromatography (TLC) was carried out on Merck 1.05554 aluminum sheets precoated with silica gel 60 F254 and the spots were visualized with UV light at 254 nm or under iodine. Column chromatography purifications were performed by using Merck silica gel 60 (0.063-0.200 mm). Elemental analysis (C, H, N, S)

were done on a Vario EL III Elemental analyzer. Infrared spectra of the ligands and the metal complexes were recorded as KBr discs in the range of 4000−400 cm^{-1} using a Nicolet Avatar model FT-IR spectrophotometer. ^{1}H (300 and 400 MHz), ^{13}C (100 MHz) and ^{31}P NMR (162 MHz) spectra were taken in DMSO-d_6 or $CDCl_3$ at room temperature with a Bruker AV400 instrument with chemical shifts relative to tetramethylsilane (^{1}H, ^{13}C) and *o*-phosphoric acid (^{31}P). Mass spectra were drawn on a LC−MS Q−ToF Micro Analyzer (Shimadzu), using electrospray ionization (ESI) mode. The melting points were checked with a Lab India melting point apparatus.

Crystals of **2** and **3** were mounted on glass fibers and used for data collection. Crystal data were collected at 295 K using a Gemini A Ultra Oxford Diffraction automatic diffractometer. Graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) was used throughout. The absorption corrections were performed by the multi-scan method. Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods using the program SHELXS [44]. Refinement and all further calculations were carried out using SHELXL. The H atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least squares on F^2. In the solid state, a disorder is observed within the two different enantiomeric forms in such a manner that only the carbonyl group and the chlorine atom share the ligand positions mutually. The reported method was used for the synthesis of $[RuHClCO(AsPh_3)_3]$ [45] and *cis*-$[RuCl_2(dmso)_4]$ [46].

2.2 Synthesis of 2-(2-(diphenylphosphino)benzylidene)-2-thiophenecarboxylic acid hydrazone (PNO-THy) ligand

To a solution of 2-(diphenylphosphino)benzaldehyde (0.290 g, 1 mmol) and 2-thiophene carboxylic acid hydrazide (0.126 g, 1 mmol) in ethanol (20 mL) were added 2−3 drops of glacial acetic acid. The resulting solution was heated under reflux over a 3 h period, and then concentrated to *ca*. 3 mL. The white crystalline precipitate was filtered off, washed with diethyl ether (2 x 5 mL), and dried under *vacuo*. Yield: 87% (0.36 g). Mp: 197−199 °C. Anal. Calcd for $C_{24}H_{19}N_2OPS$: C, 69.55; H, 4.62; N, 6.76; S, 7.74. Found: C, 69.67; H, 4.58; N, 6.86; S, 7.69. IR (KBr disks, cm^{-1}): 3195 (m, ν_{NH}); 1685 (s, $\nu_{C=O}$); 1583 + 1474 (s, $\nu_{C=N}$ + ν_{C-N}). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 6.83−7.50 (m, 14H, Ar H), 7.57 (t, 1H, J = 6.24, Hz Ar H), 8.05 (s, 1H,

Ar H), 8.15 (s, 1H, Ar H), 8.85 (d, IH, J = 3.6 Hz, −CH=N), 9.13 (s, 1H, Ar H), 11.98 (s, IH, −NH). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 125.78 (Ar C), 128.91 (Ar C), 129.15 (Ar C), 129.47 (Ar C), 130.07 (Ar C), 133.30 (Ar C), 133.49 (Ar C), 134.12 (Ar C), 135.62 (Ar C), 138.25 (Ar C), 149.52 (−CH=N), 158.12 (C=O). ^{31}P NMR (162 MHz, DMSO-d_6, ppm): −17.14.

2.3 Synthesis of 2-(2-(diphenylphosphino)benzylidene)-4-phenyl-3-thiosemicarbazone (PNS-Ph) ligand

To a solution of 2-(diphenylphosphino)benzaldehyde (0.290 g, 1 mmol) and 4-phenyl-3-thiosemicarbazide (0.167 g, 1 mmol) in ethanol (20 mL) were added 2−3 drops of glacial acetic acid. The pale yellow solution was heated under reflux over a 2 h period, and then concentrated to dryness. The resulting yellow oil was treated with diethyl ether (2 x 5 mL). The pale yellow precipitate was filtered off, washed with diethyl ether (10 mL) and dried under *vacuo*. Mp: 198 °C. Anal. Calcd for $C_{20}H_{18}N_3P_2S$: C, 60.91; H, 4.60; N, 10.65; S, 8.13%. Found: C, 60.99; H, 4.62; N, 10.60; S, 8.16%. IR (KBr disks, cm^{-1}): 3303 (m, ν_{NH}); 1594 + 1546 (s, $\nu_{C=N} + \nu_{C-N}$); 744 (s, $\nu_{C=S}$). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 6.80 (t, 1H, J = 4.8, Ar H), 7.16−7.45 (m, 12H, Ar H), 7.52 (d, 2H, J = 7.6 Hz, Ar H), 8.31−8.34 (m, 1H, $-NH_{terminal}$), 8.79 (d, 1H, J = 4.4 Hz, −CH=N), 11.94 (s, 1H, $-NH_{hydrazinic}$). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 125.26 (Ar C), 125.55 (Ar C), 127.44 (Ar C), 128.01 (Ar C), 128.78 (Ar C), 128.85 (Ar C), 129.01 (Ar C), 129.12 (Ar C), 129.87 (Ar C), 132.94 (Ar C), 133.36 (Ar C), 133.56 (Ar C), 135.60 (Ar C), 135.70 (Ar C), 136.05 (Ar C), 136.24 (Ar C), 137.24 (Ar C), 137.43 (Ar C), 138.82 (Ar C), 141.07 (−CH=N), 175.81 (C=S). ^{31}P NMR (162 MHz, DMSO-d_6, ppm): −11.12.

2.4 Synthesis of [Ru(PNO-THy)$_2$] **(1)**

A suspension of $[RuCl_2(dmso)_4]$ (0.2 g, 0.44 mmol) in CH_2Cl_2 (20 mL) was treated with PNO-THy (0.364 g, 0.88 mmol) in ethanol (30 mL) and the mixture was gently refluxed for 6 h. During this time the color changed to dark red. The solvent was removed on a rotary evaporator. The residue was then chromatographed on alumina oxide with ethyl acetate/petroleum ether. A red band was eluted with 6:4 ethyl acetate/ petroleum ether mixture and it was identified as **1** (yield 78%). Mp: 259 °C. Anal. Calcd for $C_{48}H_{36}N_4O_2P_2RuS_2$: C, 62.13; H, 3.91; N, 6.04; S, 6.91%. Found: C, 62.31; H, 3.98; N, 6.24; S, 6.98%. IR (KBr disks, cm^{-1}): 3441, 3204 (m, ν_{NH}); 1572 + 1481 (s, $\nu_{C=N} + \nu_{C-N}$), 1276 (s, ν_{C-O}). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 6.57 (m, 4H,

J = 7.2 Hz, Ar H), 6.70 (t, 2H, *J* = 8.8 Hz, Ar H), 6.84 (t, 6H, *J* = 7.2 Hz, Ar H), 7.75−7.02 (m, 18H, Ar H), 7.86 (t, 2H, *J* = 7.2 Hz, Ar H), 8.46 (d, 2H, *J* = 8.3 Hz, −CH=N). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 128.00 (Ar C), 128.10 (Ar C), 128.41 (Ar C), 128.64 (Ar C), 129.06 (Ar C), 129.89 (Ar C), 130.32 (Ar C), 130.48 (Ar C), 131.03 (Ar C), 131.29 (Ar C), 131.38 (Ar C), 131.68 (Ar C), 131.79 (Ar C), 132.80 (Ar C), 132.91 (Ar C), 133.12 (Ar C), 133.54 (Ar C), 133.79 (Ar C), 133.90 (Ar C), 134.00 (Ar C), 138.91 (C=N), 161.80 (C−O). ^{31}P NMR (162 MHz, DMSO-d_6, ppm): 29.12 (s, PPh_2). ESI-MS: *m*/*z* = 927.81 $[M]^+$.

2.5 Synthesis of [Ru(PNS-Ph)$_2$] **(2)**

A suspension of $[RuCl_2(dmso)_4]$ (0.2 g, 0.44 mmol) in CH_2Cl_2 (20 mL) was treated with PNS-Ph (0.386 g, 0.88 mmol) in ethanol (30 mL) and the mixture was gently refluxed for 6 h. During this time the colour changed to dark red. The solvent was removed on a rotary evaporator. The residue was then chromatographed on alumina oxide with ethyl acetate/ petroleum ether. A red band was eluted with 6:4 ethyl acetate/ petroleum ether mixture and it was identified as **2** (65%). Single crystals of **2** were obtained by slow diffusion of diethyl ether into a saturated solution of the complex in ethyl acetate. Mp: 262 °C. Anal. Calcd for $C_{52}H_{42}ClN_6OP_2RuS_2$: C, 63.86; H, 4.33; N, 8.59; S, 6.56%. Found: C, 63.92; H, 4.38; N, 8.66; S, 6.26%. IR (KBr discs, cm^{-1}): 3430, 3204 (m, ν_{NH}); 1574 + 1482 (s, $\nu_{C=N} + \nu_{C-N}$); 749 (s, ν_{C-S}). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 6.55 (t, 2H, *J* = 8.0 Hz, Ar H), 6.45 (t, 2H, *J* = 8.0 Hz, Ar H), 6.62 (t, 1H, *J* = 7.6 Hz, Ar H), 6.89−6.86 (m, 1H, Ar H), 7.63−7.10 (m, 8H, Ar H), 7.91 (s, 1H, $NH_{terminal}$), 8.41 (d, 1H, *J* = 8.1 Hz, −CH=N). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 125.26 (Ar C), 125.55 (Ar C), 127.44 (Ar C), 128.01 (Ar C), 128.78 (Ar C), 128.85 (Ar C), 129.01 (Ar C), 129.12 (Ar C), 129.87 (Ar C), 132.94 (Ar C), 133.36 (Ar C), 133.56 (Ar C), 135.60 (Ar C), 135.70 (Ar C), 136.05 (Ar C), 136.24 (Ar C), 137.24 (Ar C), 137.43 (Ar C), 138.82 (Ar C), 138.91 (Ar C), 140.13 (−CH=N), 170.12 (C−S). ^{31}P NMR (162 MHz, DMSO-d_6, ppm): δ 28.78 (s, PPh_2). ESI-MS: *m*/*z* = 978.57 $[M]^+$.

2.6 Synthesis of [RuCl(CO)(AsPh$_3$)(PNO-THy)] **(3)**

A suspension of $[RuHCl(CO)(AsPh_3)_3]$ (0.2 g, 0.184 mmol) in ethanol (30 mL) was treated with 2-(2-(diphenylphosphino)benzylidene)-2-thiophene carboxylic acid hydrazone (0.072 g, 0.184 mmol) and the mixture was gently refluxed for 8h. During this time the color

changed to orange. The solvent was reduced to half of the volume on a rotary evaporator, and the suspension was filtered, washed thoroughly with cold ethanol (10 mL) and diethyl ether (2 x 20 mL). The product was finally dried under *vacuo*. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated solution of **3** in CH_2Cl_2/C_2H_5OH. Yield 81% (0.163 g), Mp: 120−122 °C. Anal. Calcd for $C_{43}H_{33}AsClN_2O_2PRuS$: C, 58.41; H, 3.76; N, 3.17; S, 3.63. Found: C, 58.62; H, 3.82; N, 3.31 S, 3.69. IR (KBr disks, cm^{-1}): 3323 (m, ν_{NH}); 1946 (s, $\nu_{C\equiv O}$); 1592 + 1480 (s, $\nu_{C=N}$ + ν_{C-N}); 1274 (s, ν_{C-O}); 1432, 1091, 695 (s, for $AsPh_3$). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 6.37 (td, 1H, J = 7.2, 1.2 Hz, Ar H), 7.10−7.52 (m, 29H, Ar H), 7.67 (dd, 1H, J = 3.6, 1.2 Hz, Ar H), 8.12 (d, IH, J = 3.6 Hz, −CH=N), 8.93 (s, 1H, Ar H). ^{13}NMR (100 MHz, DMSO-d_6, ppm): 124.10 (Ar C), 128.50 (Ar C), 128.67 (Ar C), 129.92 (Ar C), 130.5 (Ar C), 133.80 (Ar C), 133.20 (Ar C), 133.41 (Ar C), 133.560 (Ar C), 133.92 (Ar C), 143.40 (CH=N), 149.23 (C−O), 200.12 (C≡O). ^{31}P NMR (162 MHz, DMSO-d_6, ppm): 32.19 (s, PPh_2). ESI-MS: m/z = 848.57 $[M–Cl]^+$.

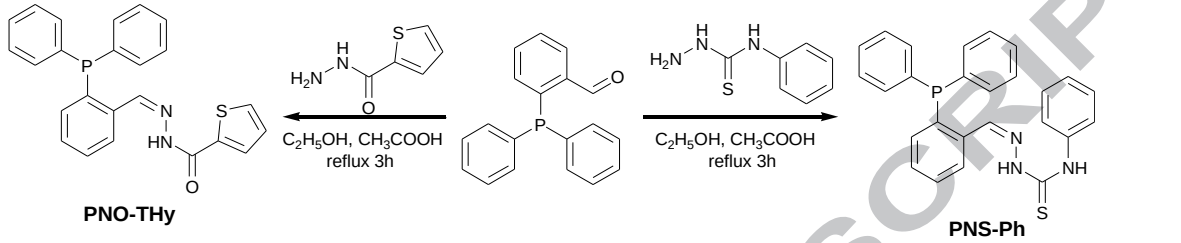
2.7 Typical procedure for N-alkylation of (hetero)aromatic amines with alcohols

In a 25 mL round bottomed flask were placed 0.5 mol % of ruthenium(II) catalyst, 2 mmol of alcohol, 2 mmol of amine, 50 mol % of KOH and 2 mL of toluene. The reaction flask was heated at 100 °C for 12 h in an oil bath. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H_2O (3 mL) was added and the organic layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with magnesium sulfate and concentrated. The crude product was purified by column chromatography (ethyl acetate/*n*-hexane). Reported isolated yields are an average of two runs.

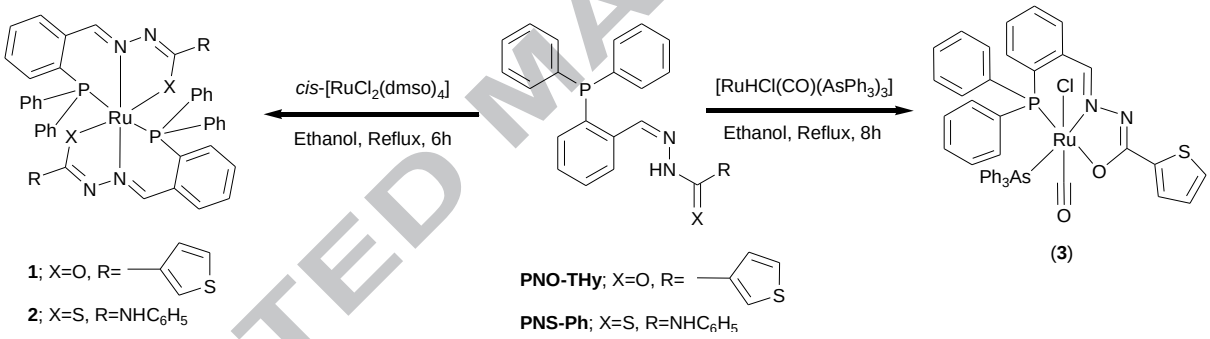
3. Results and discussion

The ligand precursors (PNO-Thy and PNS-Ph) were synthesized by condensation of 2-diphenylphosphinebenzaldehyde with 2-thiophenecarboxylic acid hydrazide and 4-phenyl-3-thiosemicarbazide respectively, following the published procedure (Scheme 1) [47]. The reactions of the isolated ligands with equimolar amounts of *cis*-$[RuCl_2(dmso)_4]$ and $[RuHCl(CO)(AsPh_3)]$ yielded the substituted products **1**-**3** respectively (Scheme 2). These Ru complexes are air stable, were obtained in good yield (64–85%), and were characterized by analytical, spectroscopic methods (IR, ^{1}H, ^{13}C, ^{31}P-NMR and ESI-MS) and X-ray

crystallography for **2** and **3** as described further below. The analytical data of the complexes agreed well with the proposed molecular formulae. Positive ion ESI-MS analysis of the isolated products showed an intense peak for $[M]^+$ (*m/z* 927.81(**1**), *m/z* 978.57 (**2**)) or $[M-Cl]^+$ (*m/z* 848.57 (**3**), which confirming the proposed nature of these complexes.



Scheme 1 Synthesis of phosphino hydrazone and thiosemicarbazone ligands.



Scheme 2 Synthesis of ruthenium(II) complexes.

3.1 Crystal structure of the complexes

The crystal structure of the complexes **2** and **3** along with their numbering scheme are given in figures 1 and 2. Crystallographic data and bond parameters are given in table 1. Single crystals of **2** were obtained by slow diffusion of diethylether into a saturated solution of the complex in ethyl acetate. A dark red crystal of approximate dimensions 0.23 x 0.04 x 0.03 mm was isolated and the single crystal X-ray diffraction experiments were carried out at 295 K. From the unit cell dimensions, it is clear that the crystal is monoclinic belonging to the *I*12/a1 space group. The two PNS-Ph ligands around the metal centre in **2** are arranged in a *mer–mer*

configuration with the two nitrogen atoms *trans* to one another and the two phosphorus and two sulfur atoms in a *cis* configuration. The average Ru–P, Ru–N and Ru–S bond lengths in **2** are 2.30, 2.06 and 2.37 Å respectively, which compare well to those observed in related Ru^{II} complexes [43a] The average *cis* angles are S(1)−Ru(1)−S(1) = 87.24(8)°, P(1)−Ru(1)−S(1) = 88.66(5)°, P(1)−Ru(1)−P(1), 98.12(5)°, N(1)−Ru(1)−S(1) = 91.35(8)° and N(1)−Ru(1)−P(1) = 93.10(8)° respectively. The *trans* angles P(1)−Ru(1)−S(1) = 173.21(3)° and N(1)−Ru(1)−N(1) = 169.95(16)° deviate from linearity. The variations in bond lengths and angles lead to a significant distortion from an ideal octahedral geometry for the complex.

The complex **3** was crystallized in monoclinic crystal system with the space group P2(1). The phosphino hydrazone ligand is coordinated to ruthenium by utilizing its phosphorous, azomethine nitrogen and hydrazone oxygen atom. The O(2)-Ru(1)-P(1) [170.73(7)°], N(1)-Ru(1)-As(1) [164.12(8)°] and C(1)-Ru(1)-Cl(1) [174.11(11)] *trans* angles deviate significantly from linearity and N,O chelation (five member ring) leads to N(1)-Ru(1)-O(2) bite angle, 77.68(10)°. This has resulted in significant distortion in RuCONOPAs core from the ideal octahedral geometry. All the Ru-ligand distances, namely Ru(1)-C(1) 1.936(4) Å, Ru(1)-N(1) 2.061 (3) Å, Ru(1)-P(1) 2.2969(9) Å, Ru(1)-O(2) 2.099 (2) Å, Ru(1)-As(1) 2.4777 (6) Å and Ru(I)-Cl(1) 2.4061(10) Å are comparable with those found in complexes reported earlier. The large deviation of the [P(1)−Ru(1)−P(2)] angle [99.78(3)] from 90 may be ascribed to the steric repulsion between the two adjacent bulky phosphine and arsine molecules.

3.2 Spectral studies

The IR spectra of the ligands and the corresponding complexes provided significant information's about the metal ligand bonding. A strong vibration observed at 1594−1583 cm^{-1} in the ligands corresponding to $\nu_{C=N}$ was shifted to 1592−1572 cm^{-1} in all the complexes indicating the participation of azomethine nitrogen in bonding [43c]. A sharp band observed at 1685 cm^{-1} and 744 cm^{-1} ascribed to $\nu_{C=O}/\nu_{C=S}$ in the ligands, has completely disappeared in the spectra of the new Ru complexes and the appearance of a new band at 1276-1274 cm^{-1} and 749 cm^{-1} due to ν_{C-O}/ν_{C-S} indicate the coordination of the oxygen/sulfur atom after enolisation followed by deprotonation [48]. The complex **3** displayed a medium to strong band in the region 1946 cm^{-1}, which is attributed to the terminally coordinated carbonyl group and is observed at a slightly higher frequency than in the precursor complexes. The IR spectra of all the complexes therefore

confirms the coordination mode of the phosphino-hydrazone/thiosemicarbazone ligand to the ruthenium(II) ion via the azomethine nitrogen, the imidolate oxygen/thiolate sulfur and the phosphorous, along with the presence of triphenylarsine group.

The ^{1}H NMR spectra of the ligands and their complexes (**1**−**3**) show the signals in the expected regions. The singlet's that appeared for the N–NH–C=X (X=O or S) proton of the free ligands at 11.98−11.94 ppm are absent in the complexes, supporting the enolization and coordination of the imidolate oxygen or thiolate sulphur to the Ru(II) ion. The doublet due to azomethine proton (8.46−8.12 ppm) in the complexes are slightly downfield compared to the free ligands (8.85−8.79 ppm), suggesting deshielding upon coordination to Ru(II) ion. The ^{13}C NMR spectra show the expected signals in the appropriate regions. For the uncoordinated ligands, the C=N and C=O/C=S signals appear in the regions around 149.52−141.07 ppm and 158.12/175.81 ppm. Upon coordination and formation of the new Ru complexes, a downfield shift is observed for the signals of the C=N (143.40-138.91ppm), while the C-O/C-S carbon atom signals are appeared in the region between 161.80−149.23 and 170.12 ppm. This is consistent with the PNO/PNS coordination and enolization of the C=O/C=S of hydrazone and thiosemicarbazone moieties. The C≡O carbon resonating at 200.12 ppm is comparable with earlier observations (for complex **3**) [43b]. The presence of a residual phosphine coordinated to Ru(II) ion is confirmed by ^{31}P NMR. The singlet observed at 32.19−28.78 ppm in complexes **1**–**3**, suggested the presence of phosphine heads in the hydrazone and thiosemicarbazone chains. These signals are very significantly shifted downfield compared with the corresponding free ligands (~40 ppm), being indicative of coordination through to the phosphorus atom [7].

3.3 Catalytic N-alkylation of amines

Initial studies were performed using 2-aminobenzothiazole and benzyl alcohol as building blocks and toluene as the solvent, under various reaction conditions and the results are depicted in Table 3. To ensure its catalytic role, a control experiment was performed in the absence of base or ruthenium catalyst and, as expected, there was no reaction even after a prolonged reaction time of 12 h (entries 1 and 9). Using K_2CO_3, Na_2CO_3, NaOH and KO*t*Bu as alternative base for the reaction, decreases in the yield were observed (entries 2–4 and 8). Furthermore, considering the results when 0.5 mol% of catalyst was used, it is clear that ruthenium complexes containing phosphino hydrazone ligand (Entry 11) lead to higher yields

than the other two ruthenium catalysts (Entries 6 and 10). This behavior indicates that the steric effects or the lack of a vacant coordination site due to bischelation of ligands around the metal centre may play an important role in terms of catalyst efficiency or in terms of generation of the catalytically active species.

On the basis of the results obtained complex **3** shows relatively better catalytic activity among the three complexes. Hence, complex **3** was selected as the model catalyst for the regioselective *N*-alkylation of various heterocyclic amines, diamines with alcohols to afford the corresponding secondary amines; the results are summarized in Table 4. When an equimolar solution of 2-aminobenzothiazoles and 4-methylbenzyl alcohol with 0.5 mol % of **3** in toluene was used, the reaction went smoothly to afford the expected *N*-(4-methylbenzyl)benzo[d]thiazol-2-amine in excellent isolated yield (86%). 2-aminobenzothiazoles efficient alkylated with benzylalcohol containing electron-donating substituents. The reaction of 2- aminobenzothiazoles with 4-methoxybenzyl alcohol gave *N*-(methoxybenzo[d] thiazol-2-amine in 81% isolated yield. Similarly, the *N*-alkylation of 2- aminobenzothiazoles and 4-chlorobenzyl alcohol yielded *N*-(4-chlorobenzyl)benzo[d]thiazol-2-amine (98%). The *N*-alkylation with 2-bromo benzyl alcohol proceeded to give the corresponding product with excellent yield as well (72%). The reaction was also applied to 2-pyridylmethanol, affording the desired product with 96% yield. The compatibility of the catalytic system with heterocyclic diamine was demonstrated, and very good result was obtained for the *N,N'*-dialkylation of 2,6-diaminopyridine (Entry 4) with benzylalcohol using the catalyst **3**. Reaction of *o*-phenylenediamine with benzyl alcohol afforded the desired 2-substituted benzimidazole in 76% (Entry 5) isolated yield.

A possible catalytic cycle is proposed in Scheme 3 on the basis of the results obtained and available literature on similar ruthenium-catalyzed transformations [40]. This catalysis is considered to proceed via the (benzyloxy)ruthenium intermediate **I**, which undergoes β-hydrogen elimination to give the ruthenium hydride **II** and R_1CHO. Dehydrative condensation of R_1CHO with amine forms $R_1CH{=}NR_2$. Insertion of $R_1CH{=}NR_2$ into the Ru−H bond of **II**, followed by alcoholysis of the resulting (amido)ruthenium species **III**, affords $R_1CH_2NHR_2$ as the *N*-alkylation product and reproduces the (benzyloxy)ruthenium intermediate **I** and completes the catalytic cycle.

4. Conclusions

Three new ruthenium(II) phosphino-hydrazone/thiosemicarbazone complexes have been designed and synthesized by the reactions of *cis*-[$RuCl_2(dmso)_4$] or [$RuHCl(CO)(AsPh_3)_3$] with deprotonated PNO-THy/PNS-Ph. The structure of the complexes (**2** and **3**) were established by X-ray crystallography and spectroscopic methods. Single crystal XRD upshots of complexes revealed a distorted octahedral geometry around the ruthenium ion with hydrazone/thiosemicarbazone acts as a monoanionic tridentate PNS donor fashion. The catalytic study of complexes **1-3** towards regioselective *N*-alkylation reactions amines was completed, showing that all catalysts are active toward catalytic transformations. Notably, complex **3** was found to be very efficient catalysts toward *N*-alkylation of a wide range of heterocyclic amines with alcohols. This catalysis provides a clean, convenient and practical route for the direct *N*-alkyl amine synthesis in view of the following advantages: (1) The reaction proceeds smoothly and effectively under mild conditions. (2) The catalyst is readily available, cheap and stable that offers easy handling and ready work-up. (3) The present method is applicable in the synthesis of various *N*-alkyl amines, including useful aromatic and heteroaromatic amines, in high yields.

Acknowledgment

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Appendix A. Supplementary data

Experimental procedure and spectral data for *N*-alkylated products. CCDC reference number 1588881 and 1588827 for complexes **2** and **3**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://

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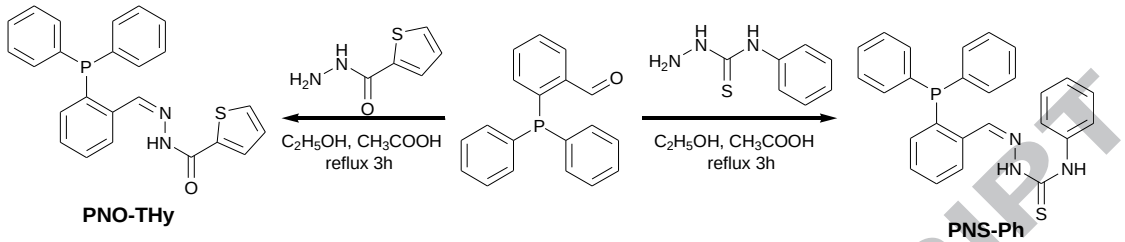
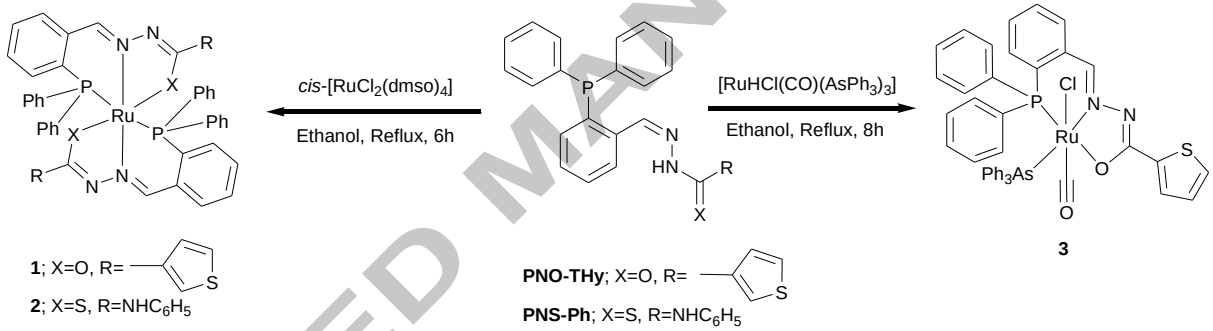


Scheme 1. Synthesis of phosphino-hydrazone and thiosemicarbazone ligands.



Scheme 2. Synthesis of ruthenium(II) complexes.

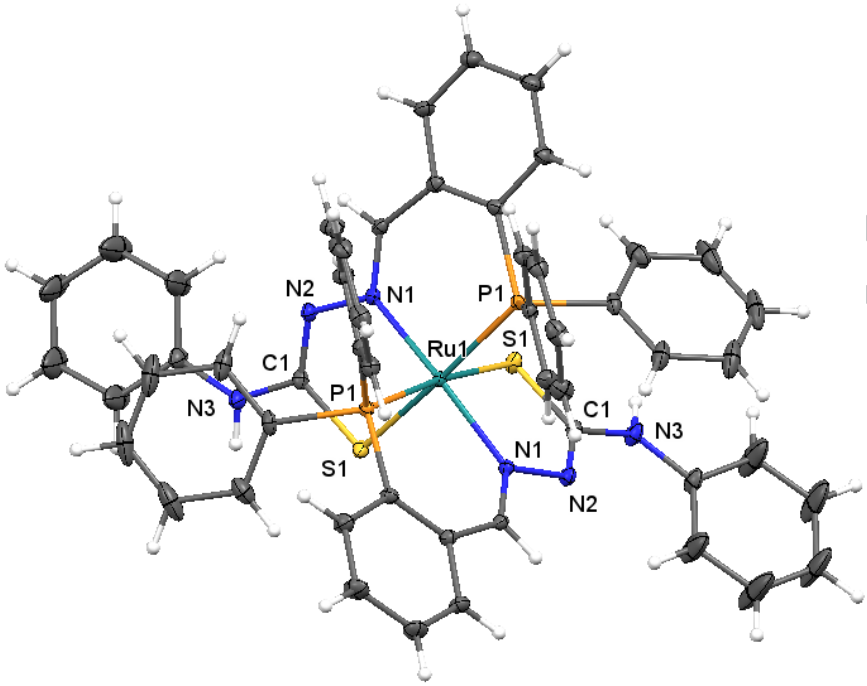


Fig. 1. Molecular structure of [Ru(PNS-Ph)$_2$] (**2**) with thermal ellipsoids at the 50 % probability level.

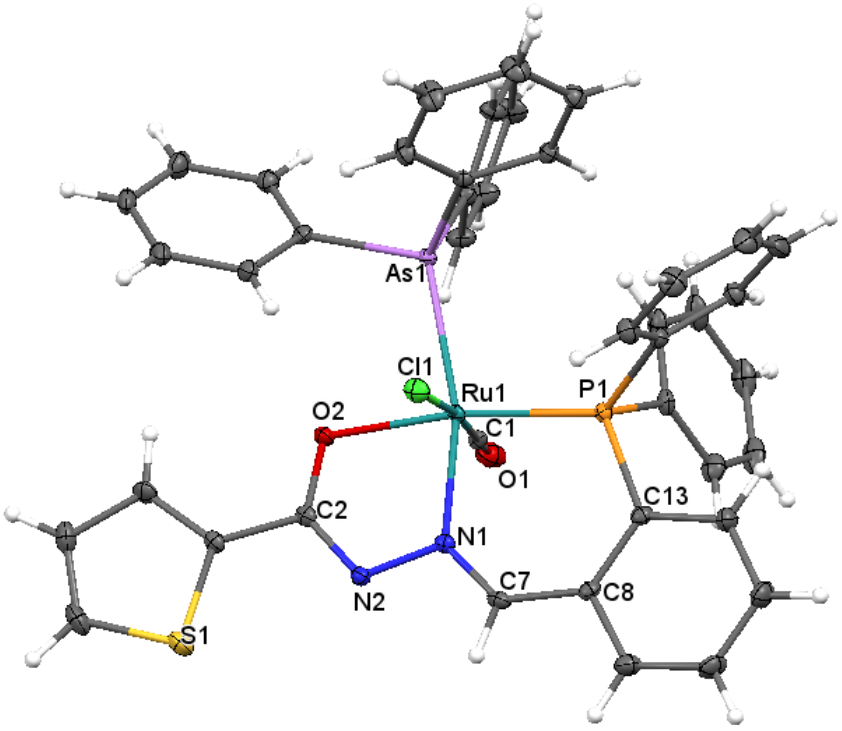
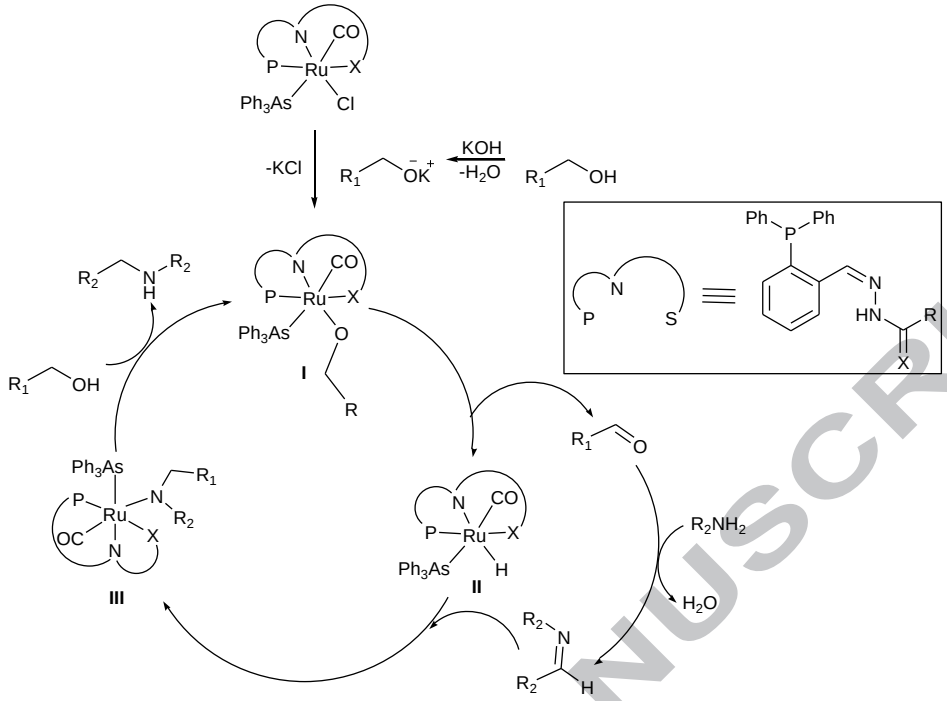


Fig. 2. Molecular structure of [RuCl(CO)($AsPh_3$)(PNO-THy)] **(3)** with thermal ellipsoids at the 50 % probability level. The disordered chloride, carbonyl and thiophene group of the structure have been omitted for clarity.

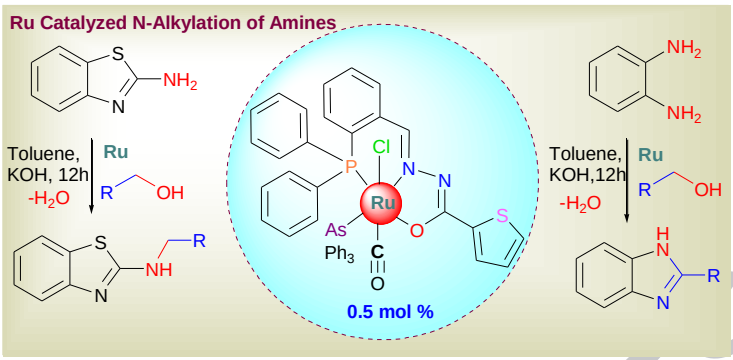


Scheme 3. Plausible mechanism for *N*-alkylation of amines.

Highlights

- Ru(II) complexes with PNO/PNS donor ligands were designed and synthesized.
- The complexes efficiently catalyzed the *N*-alkylation of amines with alcohols.
- Water as a sole by product in this novel catalytic reactions.

Graphical Abstract Pictogram



Graphical Abstract Synopsis

Ruthenium(II) complex bearing PNO ligand efficiently catalyses the *N*-alkylation of amines with alcohols. The reaction works under mild condition with 0.5 mol % of catalyst and could be performed on a small scale, providing an alternative to conventional alkylation reaction.

Highlights

- Ru(II) complexes with PNO/PNS donor ligands were designed and synthesized.
- The complexes efficiently catalyzed the *N*-alkylation of amines with alcohols.
- Water as a sole by product in this novel catalytic reactions.

Table1 Crystal, measurement and refinement data for complexes **2** and **3**

	2	**3**
Formula	$C_{52}H_{42}N_6P_2RuS_2$	$C_{43}H_{33}AsClN_2O_2PRuS$
Fw	978.04	884.18
Cryst syst	monoclinic	Triclinic
Space group	*I* 1 2/a 1	*P*Ī
a, Å	18.1577(4)	11.1690(3)
b, Å	11.2930(3)	18.3688(8)
c, Å	22.6297(5)	20.2066(6)
α, deg	90	68.206(3)
β, deg	101.712()	87.070(2)
γ, deg	90	77.349(3)
Vol, $Å^3$	4543.7(2)	3753.8(2)
Z	4	4
F(000)	2008	1784
D_{calcd}, g cm^{-3}	1.430	1.565
Absorption coefficient mm^{-1}	4.661	1.565
Scan range for data collection (deg)	4.3850 < 2θ > 67.4040	3.58 to 29.14
Index ranges	-21< = h< = 17 -13< = k< = 13 -17< = l< = 26	-11< = h< = 13 -16< = k< = 21 -24< = l< = 23
Reflections collected/unique, R_{int}	24015, 12983, 0.0548	29559/13249,0.0361
Completeness to $theta_{max}$	0.978	0.997
Data/restraints/parameters	3654/0/273	13249/0/990
Goodness-of-fit on F^2	1.081	1.033
Final *R* indices [$I > 2\sigma(I)$][a]	0.0430, 0.1261	R_1 =0.0384, wR_2 = 0.0828
R indices (all data)	0.0504, 0.1261	R_1 = 0.0584, wR_2 = 0.0828

Table 2 Selected bond lengths and bond angles for the complexes **2** and **3**

2		**3**	
Interatomic distances (Å)			
Ru(1)−C(1)	1.936(4)	Ru(1)-S(1)	2.372(8)
Ru(1)−N(1)	2.061(3)	Ru(1)-S(1)	2.3871(8)

Ru(1)−P(1)	2.2969(9)	Ru(1)-P(1)	2.3080(8)
Ru(1)−O(2)	2.099(2)	Ru(1)-P(1)	2.3080(8)
Ru(1)−As(1)	2.4777(4)	Ru(1)-N(1)	2.065(3)
Ru(1)−Cl(1)	2.4061(10)	Ru(1)-N(1)	2.065(3)
Bond angles(°)			
Cl(1)−Ru(1)−As(1)	86.26(3)	S(1)-Ru(1)-S(1)	87.24(5)
P(1)−Ru(1)−As(1)	101.14(3)	P(1)-Ru(1)-S(1)	87.46(3)
P(1)−Ru(1)−Cl(1)	94.51(3)	P(1)-Ru(1)-S(1)	173.21(3)
O(2)−Ru(1)−As(1)	88.08(6)	P(1)-Ru(1)-S(1)	173.21(3)
O(2)−Ru(1)−P(1)	170.73(7)	P(1)-Ru(1)-S(1)	172.06(5)
N(1)−Ru(1)−As(1)	164.12(8)	P(1)-Ru(1)-P(1)	98.12(4)
N(1)−Ru(1)−P(1)	93.26(8)	N(1)-Ru(1)-S(1)	90.40(8)
N(1)−Ru(1)−O(2)	77.68(10)	N(1)-Ru(1)-S(1)	92.32(8)
C(1)−Ru(1)−As(1)	96.16(10)	N(1)-Ru(1)-S(1)	82.32(8)
C(1)−Ru(1)−Cl(1)	174.11(11)	N(1)-Ru(1)-P(1)	93.10(8)
C(1)−Ru(1)−P(1)	90.30(11)	N(1)-Ru(1)-P(1)	93.10(8)
C(1)−Ru(1)−N(1)	90.35(13)	N(1)-Ru(1)-N(1)	169.95(16)

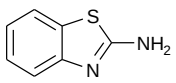
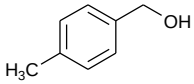
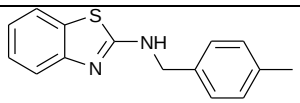
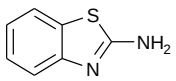
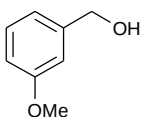
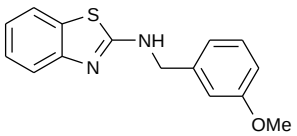
Table 3 *N*-alkylation of 2-aminobenzothiazole with benzyl alcohol under various conditions[a]

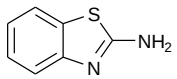
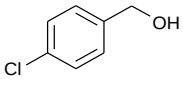
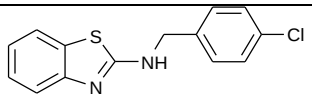
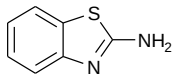
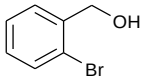
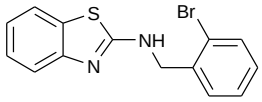
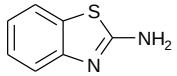
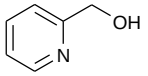
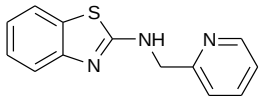
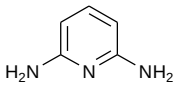
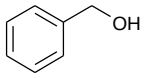
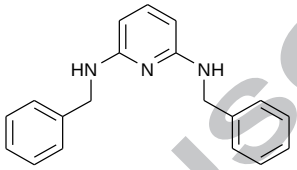
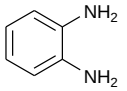
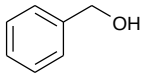
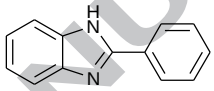
Entry	Catalyst	Catalyst (mol%)	Base	Yield (%)[b]
1	**1**	1.00	-	0
2	**1**	1.00	K_2CO_3	35
3	**1**	1.00	Cs_2CO_3	43
4	**1**	1.00	NaOH	55
5	**1**	1.00	KOH	62

6	**1**	0.50	KOH	67
7	**1**	0.25	KOH	60
8	**1**	0.50	NaO*t*Bu	51
9	-	-	KOH	0
10	**2**	0.50	KOH	64
11	**3**	0.50	KOH	92

[a]**Reaction conditions**: 2-aminobenzothiazole (1 mmol), benzyl alcohol (1 mmol), Ru catalyst, base (0.5 mmol), toluene (5 mL), at 100 ^{o}C for 12 h. [b]Isolated yield.

Table 4 *N*-alkylation of amines with various alcohols[a]

Entry	Amine	Alcohol	Product	Yield(%)[b]
1				86
2				81

3				98
4				72
5				96
6				92
7				75

[a]Reaction conditions: amine (1 mmol), alcohol (1 mmol), Ru catalyst **3** (0.50 mol%), base (0.5 mmol), toluene (5 mL), at 100 ^{o}C for 12 h. [b]Isolated yield.