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Ruthenium(II) carbonyl complexes designed with arsine and PNO/PNS ligands as catalysts for *N*-alkylation of amines via hydrogen autotransfer process

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ABSTRACT

A series of phosphine-functionalized hydrazone/thiosemicarbazone ligands and their corresponding ruthenium(II) carbonyl complexes of the type [RuCl(CO)($AsPh_3$)(**L**)] (**1-5**) [**L** = 2-(2-(diphenylphosphino) benzylidene)benzoic acid hydrazone (**PNO-BHy**), 2-(2-(diphenylphosphino)benzylidene)nicotinic acid hydrazone (**PNO-NHy**), 2-(2-(diphenylphosphino)benzylidene)-2-furoic hydrazone (**PNO-FHy**), 2-(2-(diphenylphosphino)benzylidene)-4-ethyl-3-thiosemicarbazone (**PNS-EtTs**), 2-(2-(diphenylphosphino) benzylidene)-4-cyclohexyl-3-thiosemicarbazone (**PNS-CyTs**)] have been synthesized based on the ligands with different electronic and steric effects. These complexes were characterized by elemental analyses and various spectral methods. The solid-state structure of the complex **4** was determined by single-crystal X-ray diffraction method. In all of the complexes, the ligand was bound to the Ru(II) center via the PNO/PNS donor atoms. All the ruthenium(II) complexes were demonstrated as highly efficient catalysts for the synthesis of secondary amines/amides by the coupling of primary amines/amides with alcohols at low catalyst loading, and the maximum yield was obtained up to 98%. The *N*-alkylation reaction can be readily carried out under moderate conditions, and release of water is the sole byproduct. In addition, the effects of substituents on the ligand, solvents, base and catalyst loading on the catalytic activity of the complexes have been investigated. Advantageously, only one equivalent of the alcohol was consumed in the process.

1. Introduction

Multidentate chelate ligands which can offer a selection of hard-soft donor atoms that are capable of adapting to the character of the metal center continue to excite interest [1]. Special attention has been directed to the use of hetero-multidentate hydrazone/thiosemicarbazone ligands having both hard and soft donor atoms (e.g. XNS or XNO, X═O, N and P), since the resulting complexes often show fascinating coordination chemistry [2] or remarkable properties in catalytic [3] and biological applications [4]. Hydrazones/thiosemicarbazones functionalized with an additional donor group have become important ligands due to the potential hemilability of the new donor group, which can play a dual role in a catalyst since they can easily enable coordination sites and, at the same time, protect the coordination sites by a dynamic "on and off" chelating effect [5,6] (**I-III**, Scheme 1). This is an attractive feature for catalytic systems, as it allows for the systematic development of more active catalysts utilizing rational catalyst design. In this context, several donors such as O, N, C, S and P have been reported to functionalize hydrazones/thiosemicarbazones and showed great catalytic activities in C–X (X= C and N) coupling [7], transfer hydrogenation [8] and aldehyde to amide conversion [9]. Nevertheless, the phosphine-functionalized hydrazone and thiosemicarbazone hybrid ligands are relatively not as much investigated.

Alkylated amines are important intermediates in the bulk and fine chemical industries for the production of agrochemicals, polymers, dyes, surfactants, pharmaceuticals and biologically active compounds [10]. A variety of synthetic methods for the preparation of desired amines have been reported, such as metal-catalyzed amination of aryl halides (Buchwald–Hartwig amination) [11],

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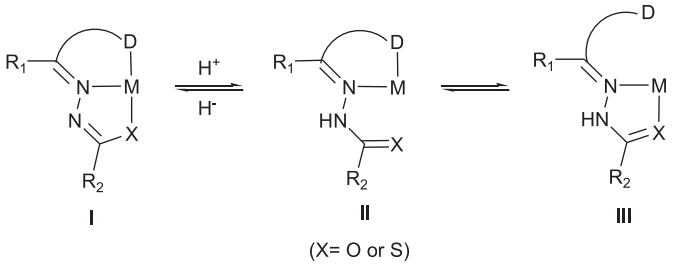


Scheme 1. Hemilability of hydrazone/thiosemicarbazone ligands in catalysis.

hydroamination [12] and hydroamino-methylation of unsaturated compounds [13], reductive amination of carbonyl compounds or reduction of imines, nitriles and nitro compounds [14]. However, these methods were associated with the side reactions, tedious work-up procedures, use of toxic reagents and formation of large amounts of inorganic salts as waste. Hence, developing more efficient and green alkylation methodologies utilizing nonhazardous and easily available starting materials would be most desirable for future sustainable processes. Recently, less toxic and more readily available alcohols were used as the alkylating agents in a greener approach using a metal catalyzed borrowing-hydrogen strategy or hydrogen autotransfer process [15]. This approach is atom economic, thermodynamically favored, proceeds with only water as by-product and follows a cascade redox type pathway involving *in-situ* alcohol oxidation/imine formation/imine hydrogenation steps. Although both heterogeneous and homogeneous catalysts have been known to promote the reaction [16–20], iridium [17] and ruthenium [18–20] complexes have constituted a vast majority of the homogeneous catalysts because of their high catalytic performance with high product selectivity [21,22]. Several iridium and ruthenium catalytic systems bearing phosphine ligands [21–27] have been reported to complete the *N*-alkylation of amines with alcohols by means of good yields and selectivity (**A-D**; Fig. 1). 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 [28]. 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 catalysts for homogeneous catalysis [29], we have disclosed that thiosemicarbazone with ONS, NNS, PNS and O_2N_2 functionalities in Ru(II) complex catalyst can show a remarkable acceleration effect on the transfer hydrogenation or *N*-alkylation amines [30]. Here, we report a series of ruthenium(II) PNO/PNS complexes (Fig. 1) in which the ligands have been varied systematically to study the influence of the oxygen/sulfur donor substituent as well as the alkyl/aryl substituent's at the terminal position on the steric and electronic properties of the metal center. The new ruthenium complexes are active toward *N*-alkylation of a wide variety of amines and amides under moderate conditions with almost quantitative conversions and short reaction times.

2. Experimental section

2.1. Physical measurements

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 using Merck silica gel 60 (0.063–0.200 mm). The ^{1}H, ^{13}C and ^{31}P NMR spectra were measured on a Bruker AV400 instrument with chemical shifts relative to tetramethylsilane (^{1}H, ^{13}C) and *o*-phosphoric acid (^{31}P) at 400, 100, and 162 MHz, respectively. The C, H, and N analyses were carried out with 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. Mass spectra were measured 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 **4** were mounted on glass fibers and used for data collection. Crystal data were collected at 295 K using a Gemini An Ultra Oxford Diffraction automatic diffractometer. Graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ 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 [31]. 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.

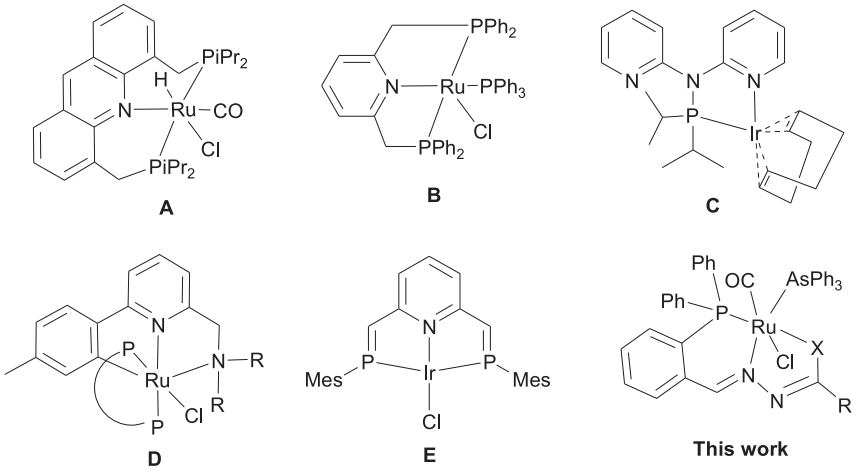


Fig. 1. Metal-phosphine based active catalysts for amine/amide synthesis. from alcohols (**A-C**) and present work.

2.2. Reagents and materials

All solvents were dried and distilled before use by standard procedures. The common reagents and chemicals available commercially within India were used. Ruthenium(III) trichloride hydrate, triphenylarsine, nicotinic acid hydrazide, 2-furoic hydrazide and 4-ethyl-3-thiosemicarbazide were procured from Sigma–Aldrich and used as received. The reported methods were used for the synthesis of 2-(diphenylphosphino)benzaldehyde [32], 2-(2-(diphenylphosphino)benzylidene)nicotinic acid hydrazone (**PNO-BHy**) [33], 4-cyclohexyl-3-thiosemicarbazide [34] and [RuHCl(CO)($AsPh_3$)$_3$] [35].

2.3. Synthesis of PNO type hydrazone ligands

To a solution of 2-(diphenylphosphino)benzaldehyde (0.290 g, 1 mmol) and nicotinic acid hydrazide (0.137 g, 1 mmol)/2-furoic 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*.

2.3.1. 2-(2-(diphenylphosphino)benzylidene)nicotinic acid hydrazone (PNO-NAHy)

Yield: 95% (0.39 g). Mp: 165–166 °C. Anal. Calcd for $C_{25}H_{20}N_2OP$: C, 73.34; H, 4.92; N, 10.26%. Found: C, 73.46; H, 4.89; N, 10.34%. IR (KBr disks, cm^{-1}): 3295 (m, ν_{NH}); 1699 (s, $\nu_{C=O}$); 1588 + 1478 (s, $\nu_{C=N} + \nu_{C-N}$). ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.37 (td, 1H, J = 1.2, 7.2 Hz, Ar H), 6.85 (td, 1H, J = 2.4, 4.8 Hz, Ar H), 7.1–7.58 (m, 11H, Ar H), 8.08 (dd, 1H, J = 3.2, 4 Hz, Ar H), 8.21 (d, 1H, J = 8 Hz, Ar H), 8.73 (d, IH, J = 3.6 Hz, −CH=N), 9.01 (s, 1H, Ar H), 9.18 (d, 1H, J = 14 Hz, Ar H), 12.12 (s, 1H, −NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 123.45 (Ar C), 125.83 (Ar C), 128.85 (Ar C), 128.91 (Ar C), 129.14 (Ar C), 129.46 (Ar C), 130.28 (Ar C), 133.25 (Ar C), 133.45 (Ar C), 135.42 (Ar C), 140.48 (Ar C), 145.99 (Ar C), 148.59 (−CH=N), 152.24 (C=O). ^{31}P NMR (162 MHz, DMSO-d_6): δ −17.06 (s, PPh_2).

2.3.2. 2-(2-(diphenylphosphino)benzylidene)-2-furoic hydrazone (PNO-FHy)

Yield: 87% (0.36 g). Mp: 211–212 °C. Anal. Calcd for $C_{24}H_{19}N_2O_2P$: C, 72.35; H, 4.81; N, 7.03%. Found: C, 72.47; H, 4.83; N, 7.12%. IR (KBr disks, cm^{-1}): 3195 (m, ν_{NH}); 1685 (s, $\nu_{C=O}$); 1583 + 1474 (s, $\nu_{C=N} + \nu_{C-N}$). ^{1}H NMR (400 MHz, DMSO-d_6): δ 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): δ 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): δ −16.84 (d, J = 97.67 Hz, PPh_2).

2.4. Synthesis of PNS type thiosemicarbazone ligands

To a solution of 2-(diphenylphosphino)benzaldehyde (0.290 g, 1 mmol) and 4-ethyl-3-thiosemicarbazide (0.119 g, 1 mmol)/4-cyclohexyl-3-thiosemicarbazide (0.173 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 1 h period, then concentrated to ca. 3 mL and cooled to 0 °C for overnight. The pale yellow precipitate was filtered off, washed with diethyl ether (2 x 5 mL) and dried under *vacuo*.

2.4.1. 2-(2-(diphenylphosphino)benzylidene)-4-ethyl-3-thiosemicarbazone (PNS-EtTs)

Yield: 97% (0.38 g). Mp: 198 °C. Anal. Calcd for $C_{22}H_{22}N_3PS$: C, 67.50; H, 5.66; N, 10.73; S, 8.19%. Found: C, 67.72; H, 5.62; N, 10.74; S, 8.26%. IR (KBr disks, cm^{-1}): 3326 (m, ν_{NH}); 1584 + 1478 (s, $\nu_{C=N} + \nu_{C-N}$); 744 (s, $\nu_{C=S}$). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.07 (t, 3H, J = 7.2 Hz, $-CH_3$), 3.46–3.53 (m, 2H, $-CH_2$), 6.75–6.78 (m, 1H, Ar H), 7.16–7.21 (m, 4H, Ar H), 7.31 (t, 1H, J = 7.2 Hz, Ar H), 7.39–7.45 (m, 6H, Ar H), 7.51–7.72 (m, 2H, Ar H), 8.14 (q, 1H, $-NH_{terminal}$), 8.64 (d, IH, J = 4.8 Hz, −CH=N), 11.53 (s, IH, $-NH_{hydrazinic}$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.47 ($-CH_3$), 38.14 ($-CH_2$), 127.24 (Ar C), 127.28 (Ar C), 128.64 (Ar C), 128.79 (Ar C), 128.86 (Ar C), 128.99 (Ar C), 129.09 (Ar C), 129.59 (Ar C), 131.25 (Ar C), 131.35 (Ar C), 131.75 (Ar C), 131.92 (Ar C), 133.03 (Ar C), 133.35 (Ar C), 133.55 (Ar C), 133.59 (Ar C), 133.86 (Ar C), 135.65 (Ar C), 135.83 (Ar C), 135.94 (Ar C), 137.75 (Ar C), 140.25 (−CH=N), 176.62 (C=S). ^{31}P NMR (162 MHz, DMSO-d_6): δ −14.02 (s, PPh_2).

2.4.2. 2-(2-(diphenylphosphino)benzylidene)-4-cyclohexyl-3-thiosemicarbazone (PNS-CyTs)

Yield: 93% (0.41 g). Mp: 197–198 °C. Anal. Calcd for $C_{26}H_{28}N_3PS$: C, 70.09; H, 6.33; N, 9.43; S, 7.20%. Found: C, 70.24; H, 6.21; N, 9.52; S, 7.26%. IR (KBr disks, cm^{-1}): 3343 (m, ν_{NH}); 1569 + 1475 (s, $\nu_{C=N} + \nu_{C-N}$); 748 (s, ν_{C-S}). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.32–1.23 (m, 5H, $-CH_2-$), 1.58 (d, 1H, J = 12 Hz, $-CH_2-$), 1.70 (d, 2H, J = 12 Hz, $-CH_2-$), 1.82 (d, 2H, J = 9.2 Hz, $-CH_2-$), 4.12 (s, 1H, −CH−), 6.77 (dq, 1H, J = 1.2, 3.2 Hz, Ar H), 7.14–7.21 (m, 4H, Ar H), 7.32 (td, 1H, J = 1.2, 6.4 Hz, Ar H), 7.38–7.40 (m, 6H, Ar H), 7.43 (td, 1H, J = 1.2, 6.8 Hz, Ar H), 7.79 (td, 1H, J = 8.4 Hz, Ar H), 8.09–8.06 (m, 1H, $-NH_{terminal}$), 8.62 (d, IH, J = 4 Hz, −CH=N), 11.51 (s, IH, $-NH_{hydrazinic}$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 24.82 ($-CH_2-$), 25.03 ($-CH_2-$), 31.76 ($-CH_2-$), 52.49 (−CH−), 127.62 (Ar C), 127.67 (Ar C), 128.77 (Ar C), 128.84 (Ar C), 129.04 (Ar C), 129.09 (Ar C), 129.64 (Ar C), 133.05 (Ar C), 133.37 (Ar C), 133.57 (Ar C), 135.71 (Ar C), 135.81 (Ar C), 135.91 (Ar C), 137.36 (Ar C), 137.55 (Ar C), 140.81 (−CH=N), 175.57 (C=S). ^{31}P NMR (162 MHz, DMSO-d_6): δ −13.36 (t, J = 9.4 Hz, PPh_2).

2.5. Synthesis of the complexes 1–3

A suspension of [RuHCl(CO)($AsPh_3$)$_3$] (0.100 g, 0.092 mmol) in ethanol (20 mL) was treated with 2-(2-(diphenylphosphino)benzylidene)benzoic acid hydrazone (0.037 g, 0.092 mmol) or 2-(2-(diphenylphosphino)benzylidene)nicotinic acid hydrazone (0.038 g, 0.092 mmol) or 2-(2-(diphenylphosphino)benzylidene)-2-furoic hydrazone (0.036 g, 0.092 mmol) and the mixture was gently refluxed for 8 h. 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*.

2.5.1. [(PNO-BHy)RuCl(CO)($AsPh_3$)] (**1**)

Yield 64% (0.051 g), Mp: 247–248 °C. Anal. Calcd for $C_{45}H_{35}AsClN_2O_2PRu$: C, 61.54; H, 4.02; N, 3.19%. Found: C, 61.69; H, 3.97; N, 3.22%. IR (KBr disks, cm^{-1}): 1943 (s, $\nu_{C\equiv O}$); 1584 + 1473 (s, $\nu_{C=N} + \nu_{C-N}$); 1276 (m, ν_{C-O}); 1433, 1093, 694 (s, for $AsPh_3$). ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.56 (t, 2H, J = 8.8 Hz, Ar H), 6.72–6.60 (m, 1H, Ar H), 6.89 (t, 1H, J = 7.2 Hz, Ar H), 7.63–7.10 (m, 27H, Ar H), 7.74 (d, 2H, J = 7.6 Hz, Ar H), 7.98–7.85 (m, 1H, Ar H), 8.47 (d, 1H, J = 7.2 Hz, −CH=N). ^{13}C NMR (100 MHz, DMSO-d_6): δ 115.82 (Ar C), 116.81 (Ar C), 119.02 (Ar C), 120.45 (Ar C), 120.73 (Ar C), 121.11 (Ar C), 121.20 (Ar C), 121.53 (Ar C), 121.89 (Ar C), 122.11 (Ar C), 122.36 (Ar C), 122.65 (Ar C), 123.27 (Ar C), 123.38 (Ar C), 123.55 (Ar C), 123.71 (Ar C), 124.40 (Ar C), 129.95 (Ar C), 131.17 (Ar C),

132.35 (Ar C), 133.84 (Ar C), 135.27 (Ar C), 143.34 (C═N), 148.73 (C–O), 205.45 (C≡O). ^{31}P NMR (162 MHz, DMSO-d_6): δ 39.68 (s, PPh_2). ESI$^+$-MS: m/z = 842.72 [M–Cl]$^+$.

*2.5.2. [(PNO-NHy)RuCl(CO)($AsPh_3$)] (**2**)*

Yield 76% (0.061 g), Mp: 243–244 °C. Anal. Calcd for $C_{44}H_{34}AsClN_3O_2PRu$: C, 60.11; H, 3.90; N, 4.78%. Found: C, 60.29; H, 3.98; N, 4.78%. IR (KBr disks, cm^{-1}): 1944 (s, $\nu_{C\equiv O}$); 1572 + 1480 (m, $\nu_{C=N} + \nu_{C-N}$); 1247 (s, ν_{C-O}); 1432, 1091, 695 (m, for $AsPh_3$). ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.44 (t, 1H, J = 8.4 Hz, Ar H), 6.67 (t, 1H, J = 7.2 Hz, Ar H), 7.04 (td, 1H, J = 1.6, 6 Hz, Ar H), 7.17 (td, 2H, J = 1.6, 6 Hz, Ar H), 7.26 (dd, 4H, J = 1.6, 7.2 Hz, Ar H), 7.32 (t, 1H, J = 7.6 Hz, Ar H), 7.36–7.56 (m, 16H, Ar H), 7.62 (t, 1H, J = 7.2 Hz, Ar H), 7.69–7.82 (m, 4H, Ar H), 7.87 (td, 1H, J = 1.2, 6.0 Hz, Ar H), 8.62 (d, 1H, J = 7.0 Hz, –CH═N), 9.24 (d, 1H, J = 1.5 Hz, Ar H). ^{13}NMR (100 MHz, DMSO-d_6): δ 125.83 (Ar C), 127.20 (Ar C), 128.94 (Ar C), 129.39 (Ar C), 129.80 (Ar C), 129.98 (Ar C), 131.38 (Ar C), 131.48 (Ar C), 131.83 (Ar C), 131.91 (Ar C), 132.18 (Ar C), 133.11 (Ar C), 133.22 (Ar C), 133.47 (Ar C), 133.56 (Ar C), 133.82 (Ar C) 144.40 (C═N), 149.20 (C–O), 200.21 (C≡O). ^{31}P NMR (162 MHz, DMSO-d_6): δ 40.16 (s, PPh_2). ESI$^+$-MS: m/z = 843.70 [M–Cl]$^+$.

*2.5.3. [(PNO-FHy)RuCl(CO)($AsPh_3$)] (**3**)*

Yield 81% (0.163 g), Mp: 120–122 °C. Anal. Calcd for $C_{43}H_{33}AsClN_2O_3PRu$: C, 59.49; H, 3.83; N, 3.23%. Found: C, 59.62; H, 3.82; N, 3.21%. IR (KBr disks, cm^{-1}): 3323 (m, ν_{NH}); 1946 (s, $\nu_{C\equiv O}$); 1592 + 1480 (s, $\nu_{C=N} + \nu_{C-N}$); 1267 (s, ν_{C-O}); 1432, 1091, 695 (s, for $AsPh_3$). ^{1}H NMR (400 MHz, DMSO-d_6): δ 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): δ 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), 133.50 (Ar C), 133.92 (Ar C), 143.40 (C═N), 149.20 (C–O), 200.12 (C≡O). ^{31}P NMR (162 MHz, DMSO-d_6): δ 45.19 (s, PPh_2). ESI$^+$-MS: m/z = 832.74 [M–Cl]$^+$.

*2.5.4. Synthesis of the complexes **4** and **5***

A suspension of [RuHCl(CO)($AsPh_3$)$_3$] (0.100 g, 0.092 mmol) was treated with 2-(2-(diphenylphosphino)benzylidene)-4-ethyl-3-thiosemicarbazone (0.036 g, 0.092 mmol) or 2-(2-(diphenylphosphino)benzylidene)-4-cyclohexyl-3-thiosemicarbazone (0.041 g, 0.092 mmol) in ethanol (20 mL) and the mixture was gently refluxed for 6 h. 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 (5 mL) and diethyl ether (2 x 5 mL). The product was finally dried under vacuum, affording an orange crystalline solid.

*2.5.5. [(PNS-EtTs)RuCl(CO)($AsPh_3$)] (**4**)*

Yield 85% (0.067 g), Mp: 255–256 °C. Anal. Calcd for $C_{41}H_{36}AsClN_3OPRuS$: C, 57.18; H, 4.21; N, 4.88; S, 3.72%. Found: C, 57.29; H, 4.14; N, 4.86; S, 3.84%. IR (KBr disks, cm^{-1}): 3346 (m, ν_{NH}); 1943 (s, $\nu_{C\equiv O}$); 1580 + 1482 (s, $\nu_{C=N} + \nu_{C-N}$); 741 (s, ν_{C-S}); 1432, 1091, 692 (s, for $AsPh_3$). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.10 (t, 3H, J = 7.2 Hz, –CH_3), 3.29 (d, 2H, J = 7.2 Hz, –CH_2–), 6.42 (t, 1H, J = 8.4 Hz, Ar H), 6.66 (t, 1H, J = 8.8 Hz, Ar H), 7.04 (td, 1H, J = 1.6, 6 Hz, Ar H), 7.18 (td, 2H, J = 1.6, 6 Hz, Ar H), 7.26 (dd, 4H, J = 1.6, 7.2 Hz, Ar H), 7.32 (t, 1H, J = 7.6 Hz, Ar H), 7.36–7.39 (m, 6H, Ar H), 7.47–7.56 (m, 6H, Ar H), 7.62 (t, 1H, J = 7.2 Hz, Ar H), 7.69–7.83 (m, 4H, Ar H), 7.87 (td, 1H, J = 1.2, 6.0 Hz, Ar H), 8.43 (s, 1H, –$NH_{terminal}$), 8.67 (s, IH, –CH═N). ^{13}NMR (100 MHz, DMSO-d_6): δ 14.37 (–CH_3), 24.16 (–CH_2–), 127.56 (Ar C), 127.65 (Ar C), 128.04 (Ar C), 128.64 (Ar C), 128.69 (Ar C), 128.76 (Ar C), 128.94 (Ar C), 129.39 (Ar C), 129.80 (Ar C), 129.98 (Ar C), 131.38 (Ar C), 131.48 (Ar C), 131.96 (Ar C), 131.99 (Ar C), 132.18 (Ar C), 133.10 (Ar C), 133.29 (Ar C), 133.47 (Ar C), 133.56 (Ar C), 133.82 (Ar C), 138.10 (–CH═N), 170.86 (C═S), 200.23 (C≡O). ^{31}P NMR (162 MHz, DMSO-d_6): δ 29.43 (s, PPh_2). ESI$^+$-MS: m/z = 825.72 [M–Cl]$^+$. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated solution of **4** in CH_2Cl_2/C_2H_5OH.

*2.5.6. [(PNS-CyTs)RuCl(CO)(PPh_3)] (**5**)*

Yield 72% (0.060 g), Mp: 266–267 °C. Anal. Calcd for $C_{45}H_{42}AsClN_3OPRuS$: C, 59.05; H, 4.63; N, 4.59; S, 3.50%. Found: C, 57.29; H, 4.14; N, 4.86; S, 3.84%. IR (KBr disks, cm^{-1}): 3395, 3046 (m, ν_{NH}); 1946 (s, $\nu_{C\equiv O}$); 1582 + 1480 (s, $\nu_{C=N} + \nu_{C-N}$); 747 (s, ν_{C-S}); 1432, 1091, 695 (s, for $AsPh_3$). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.06–1.22 (m, 3H, –CH_2–), 1.54 (d, 1H, J = 11.2 Hz, –CH_2–), 1.69 (s, 2H, –CH_2–), 1.87 (s, 2H, –CH_2–), 3.62 (s, 1H, –CH–), 6.43 (t, 1H, J = 8.8 Hz, Ar H), 6.65 (t, 1H, J = 8.8 Hz, Ar H), 7.03 (td, 2H, J = 2.4, 6 Hz, Ar H), 7.19 (td, 2H, J = 2.4, 6 Hz, Ar H), 7.25–7.28 (m, 13H, Ar H), 7.31 (t, 1H, J = 8 Hz, Ar H), 7.35–7.50 (m, 2H, Ar H), 8.14 (s, 1H, –$NH_{terminal}$), 8.62 (s, 1H, –CH═N). ^{13}NMR (100 MHz, DMSO-d_6): δ 24.59 (–CH_2–), 25.65 (–CH_2–), 32.24 (–CH_2–), 54.52 (–CH–), 124.81 (Ar C), 125.14 (Ar C), 127.99 (Ar C), 128.10 (Ar C), 128.41 (Ar C), 128.67 (Ar C), 128.85 (Ar C), 129.02 (Ar C), 129.52 (Ar C), 129.89 (Ar C), 130.15 (Ar C), 130.22 (Ar C), 130.47 (Ar C), 130.87 (Ar C), 131.34 (Ar C), 131.48 (Ar C), 131.82 (Ar C), 133.15 (Ar C), 133.20 (Ar C), 133.42 (Ar C), 133.87 (Ar C), 133.97 (Ar C), 134.55 (Ar C), 138.91 (–CH═N), 167.52 (C–S), 200.21 (C≡O). ^{31}P NMR (162 MHz, DMSO-d_6): δ 32.74 (s, PPh_2). ESI$^+$-MS: m/z = 879.87 [M–Cl]$^+$.

2.6. Typical procedure for catalytic N-alkylation of amines/sulfonamides with alcohols

Amine/sulfonamide (1 mmol), alcohol (1 mmol), catalyst (0.5 mol %), KOH (50 mol %) and toluene (2 mL) were placed in a 25 mL round bottomed flask and stirred on a preheated oil bath (100 °C) for 12 h. 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. The organic extract was separated, dried, and concentrated. The desired product was purified by column chromatography with n-hexane/EtOAc as eluent.

Representative spectral data for *N*-Benzylbenzo[d]thiazol-2-amine (**3a**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.59 (s, 2H, –CH_2-), 7.07 (t, J = 7.5 Hz, 1H, ArH), 7.21–7.28 (m, 2H, ArH), 7.33–7.40 (m, 5H, ArH), 7.89 (d, J = 7.9, 1H, ArH), 8.51 (t, J = 5.6 Hz, 1H, –NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 49.49, 118.97, 120.81, 121.63, 126.26, 128.96, 127.95, 127.72, 137.71, 152.81, 167.79. Assignment of signals was further confirmed by DEPT-135 and HSQC-NMR studies.

2.7. Typical procedure for catalytic N,N′-alkylation of diamines with alcohols

Diamine (1 mmol), alcohol (2 mmol), catalyst (1 mol %), KOH (50 mol %) and toluene (2 mL) were placed in a 25 mL round bottomed flask and stirred on a preheated oil bath (100 °C) for 12 h. 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 ethyl acetate. The organic extract was separated, dried, and concentrated. The desired product was purified by column chromatography with CH_2Cl_2/EtOAc as eluent.

Representative spectral data for *N,N′*-Dibenzylpyridine-2,6-diamine (**3j**)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.43 (d, J = 5.7 Hz, 4H), 4.63 (bs, 2H), 5.74 (d, J = 7.6 Hz, 2H), 7.36–7.15 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.4, 95.0, 127.2, 128.8, 139.4, 139.5, 158.2. Assignment of signals was further confirmed by DEPT-135 and HSQC-NMR studies.

The catalytic reactions given in Tables 3–6 were similarly

Table 1
Crystal measurement and refinement data for complex **4**.

[(PNS–Et)RuCl(CO)($AsPh_3$)] (4)	
Formula	$C_{41}H_{36}AsClN_3OPRuS$
Fw	861.20
Cryst syst	monoclinic
Space group	$P2_1/c$
a, Å	14.47210(10)
B, Å	16.75920(10)
C, Å	15.2758(2)
α, deg	90
β, deg	96.5563(9)
γ, deg	90
Vol, Å^3	3680.77(6)
Z	4
F(000)	1744
D_{calcd}, g cm^{-3}	1.554
Absorption coefficient mm^{-1}	1.529
Scan range for data collection (deg)	2.947 to 25.049
Index ranges	$-16 \le h \le 17$ $-19 \le k \le 19$ $-18 \le l \le 15$
Reflections collected/unique, R_{int}	47586/6507,0.0257
Completeness to $theta_{max}$	0.998
Data/restraints/parameters	6507/0/480
Goodness-of-fit on F^2	0.997
Final *R* indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0239$, $wR_2 = 0.0574$
R indices (all data)	$R_1 = 0.0338$, $wR_2 = 0.0590$

conducted. The resulting amines and amides were identified by comparison of the ^{1}H and ^{13}C NMR data with those previously reported (see Supporting Information).

3. Results and discussion

3.1. Synthesis of PNO/PNS type ligands and ruthenium(II) complexes

The ligand precursors (Fig. 2) were synthesized by the condensation of 2-diphenylphosphinebenzaldehyde with benzoic acid hydrazide, nicotinic acid hydrazide, 2-thiophenecarboxylic acid hydrazide, 4-ethyl-3-thiosemicarbazide and 4-cyclohexyl-3-thiosemicarbazide, following the published procedure [32,33]. The new Ru complexes of the type [RuCl(CO)($AsPh_3$)(**L**)] were synthesized by reacting **PNO-BHy, PNO-INHy, PNO-FHy**, **PNS-EtTs** and **PNS-CyTs** with one equivalent of [RuHCl(CO)($AsPh_3$)$_3$] in ethanol under reflux for 6–8 h (Scheme 2). These air stable Ru complexes, were obtained in good yields (64–85%), and were characterized by analytical, spectroscopic methods (IR, ^{1}H, ^{13}C, ^{31}P NMR and ESI-MS) and by X-ray crystallography for **4** 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 **1**–**5** showed an intense peak for [M–Cl]$^+$ (*m*/*z* 842 for **1**, *m*/*z* 843 for **2**, *m*/*z* 832 for **3**, *m*/*z* 825 for **4** and *m*/*z* 879 for **5**), which confirming the proposed nature of these complexes.

Table 2
Selected bond lengths and bond angles for complex **4**.

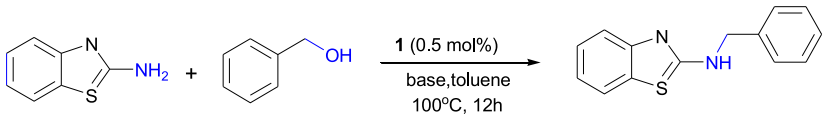
Bond length (Å)		Bond angle (°)	
Ru(1)-C(1)	1.852(9)	C(1)-Ru(1)-N(1)	86.5(3)
Ru(1)-N(1)	2.1060(18)	C(1)-Ru(1)-P(1)	90.2(3)
Ru(1)-P(1)	2.3303(6)	N(1)-Ru(1)-P(1)	91.45(5)
Ru(1)-S(1)	2.3856(7)	C(1)-Ru(1)-S(1)	89.0(3)
Ru(1)-As(1)	2.4840(3)	N(1)-Ru(1)-S(1)	81.49(6)
Ru(1)-Cl(1)	2.415(2)	P(1)-Ru(1)-S(1)	172.92(2)
C(1)-O(1)	1.132(16)	C(1)-Ru(1)-Cl(1)	172.7(3)
N(1)-N(2)	1.380(3)	N(1)-Ru(1)-Cl(1)	86.67(7)
C(4)-S(1)	1.734(3)	C(1)-Ru(1)-As(1)	96.4(3)
C(11)-P(1)	1.824(2)	N(1)-Ru(1)-As(1)	169.63(5)
C(30)-As(1)	1.961(2)	P(1)-Ru(1)-As(1)	98.466(16)
C(5)-N(1)	1.295(3)	S(1)-Ru(1)-As(1)	88.611(18)
		S(1)-Ru(1)-Cl(1)	87.45(5)
		P(1)-Ru(1)-Cl(1)	92.54(5)
		As(1)-Ru(1)-Cl(1)	89.82(5)

The IR spectra of the ligands and the corresponding complexes provided significant informations about the metal ligand bonding. A strong vibration appeared at 1588–1569 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 [36]. A sharp band was observed at 1699–1685 cm^{-1} and 748–744 cm^{-1} was ascribed to $\nu_{C=O}/\nu_{C=S}$ in the ligands which has been completely disappeared in the spectra of all the new Ru complexes and the appearance of a new band at 1276–1247 cm^{-1} and 747–741 cm^{-1} due to ν_{C-O}/ν_{C-S} indicate the coordination of the oxygen/sulfur atom after enolization followed by deprotonation [37]. All the complexes displayed a medium to strong band in the region 1946–1943 cm^{-1}, which was attributed to the terminally coordinated carbonyl group and was 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, imidolate oxygen/thiolate sulfur and the phosphorus.

The ^{1}H NMR spectra of the ligands and their complexes (**1**–**5**) have shown the signals in the expected regions. The singlets that appeared for the N–NH–C=X (X=O or S) proton of the free ligands at 12.12–11.51 ppm were 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 (8.67–8.12 ppm) in the complexes are slightly downfield compared to the free ligands (8.85–8.62 ppm), suggesting deshielding upon coordination to Ru(II) ion. The spectra of the complexes **4** and **5** showed a singlet at 8.43–8.14 ppm, which has been assigned to NH–R protons. The ^{13}C NMR spectra have shown the expected signals in the appropriate regions. For the uncoordinated ligands, the C=N and C=O/C=S signals appeared in the regions around 149.52–140.25 ppm and 158.12–152.24/176.62–175.57 ppm. Upon coordination and formation of the new Ru complexes, a downfield shift was observed for the signals of the C=N (around 5 ppm), while the C=O/C=S carbon atom signals are observed in the upfield region between 149.70 and 148.73 and 170.86–167.52 ppm. This is consistent with the PNO/PNS coordination and enolization of the C=O/C=S of hydrazone and thiosemicarbazone moieties. The peak for C≡O carbon appeared at 205.45–200.23 ppm is comparable with earlier observations [38]. In addition, a group of signal appeared around 32.24–14.37 ppm for complexes **4** and **5** corresponding to the terminal ethyl and cyclohexyl group carbon. The presence of a residual phosphine coordinated to Ru(II) ion was confirmed by ^{31}P NMR (see Supporting Information Fig. S1–S10). The singlet appeared at 45.19–32.55 ppm in complexes **1**–**5**, suggested the presence of phosphine heads in the hydrazone and thiosemicarbazone chains.

The structure of the complex [(**PNS-EtTs**)RuCl(CO) ($AsPh_3$)] (**4**) was further confirmed by single-crystal X-ray diffraction analysis of suitable crystals of **4**, grown by slow evaporation of solution of **4** in an ethanol–dichloromethane (2: 1) mixture. The crystal data and structure refinement parameters of the complex **4** have been summarized in Table 1 and the selected bond lengths and bond angles were depicted in Table 2. The ORTEP view of the complex **4** along with the atomic numbering scheme has been given in Fig. 3. The single-crystal X-ray study revealed that complex **4** is crystallized in a monoclinic system with the space group $P2_1/c$. The phosphino-

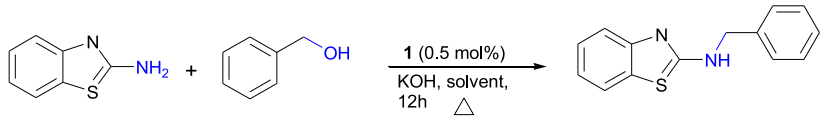
Table 3
Effect of bases on *N*-alkylation of 2-aminobenzothiazole with benzyl alcohol catalyzed by 1.[a]



Entry	Base	Amount of base (mol %)	Yield (%)[b]
1	–	–	–
2	Na_2CO_3	50	–
3	K_2CO_3	50	>2
4	KOAc	50	>5
5	NaOH	50	64
6	NaO(*t*-Bu)	50	58
7	KO(*t*-Bu)	50	71
8	KOH	20	86
9	KOH	50	94
10	KOH	100	92

[a] Reactions were carried out at 100 °C for 12 h using 2-aminobenzothiazole (1 mmol), $PhCH_2OH$ (1 mmol), **1** (0.5 mol %), and base in toluene (2 mL).
[b] Isolated yields.

Table 4
Effect of solvents on *N*-alkylation of 2-aminobenzothiazole with benzyl alcohol catalyzed by **1**.[a]

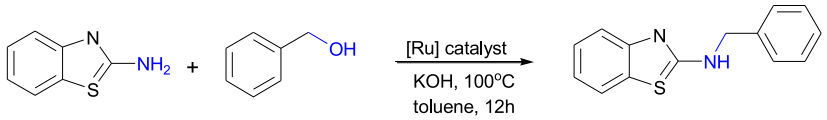


Entry	Solvent	Yield (%)[b]
1	DMF	10
2	Ethanol	18
3	Acetonitrile	25
4	Benzene	54
5	Toluene	96
6	DMSO	0
7	THF	15

[a] Reactions were carried out using 2-aminobenzothiazole (1 mmol), $PhCH_2OH$ (1 mmol), **1** (0.5 mol %) at 100 °C (for toluene, DMSO)/boiling temperature (for other solvents) (2 mL) and KOH (50 mol%).
[b] Isolated yields.

thiosemicarbazone ligand coordinated to ruthenium in PNS fashion by utilizing its phosphorous, imine nitrogen and thiolate sulfur atoms, with the formation of one six membered and another five membered ring with a N(1)–Ru(1)–S(1) bite angle of 81.49(6)° (Fig. 2). The other three sites have been occupied by arsine atom of triphenylarsine with Ru(1)–As(1) distances of 2.484(3) and one chloride and a carbonyl group with Ru(1)–Cl(1) and Ru(1)–C(1) distances of 2.415(2) and 1.852(9) Å, respectively. The observed bond distances are comparable with those found in other reported ruthenium complexes [9,30a]. The *cis* angles C(1)–Ru(1)–

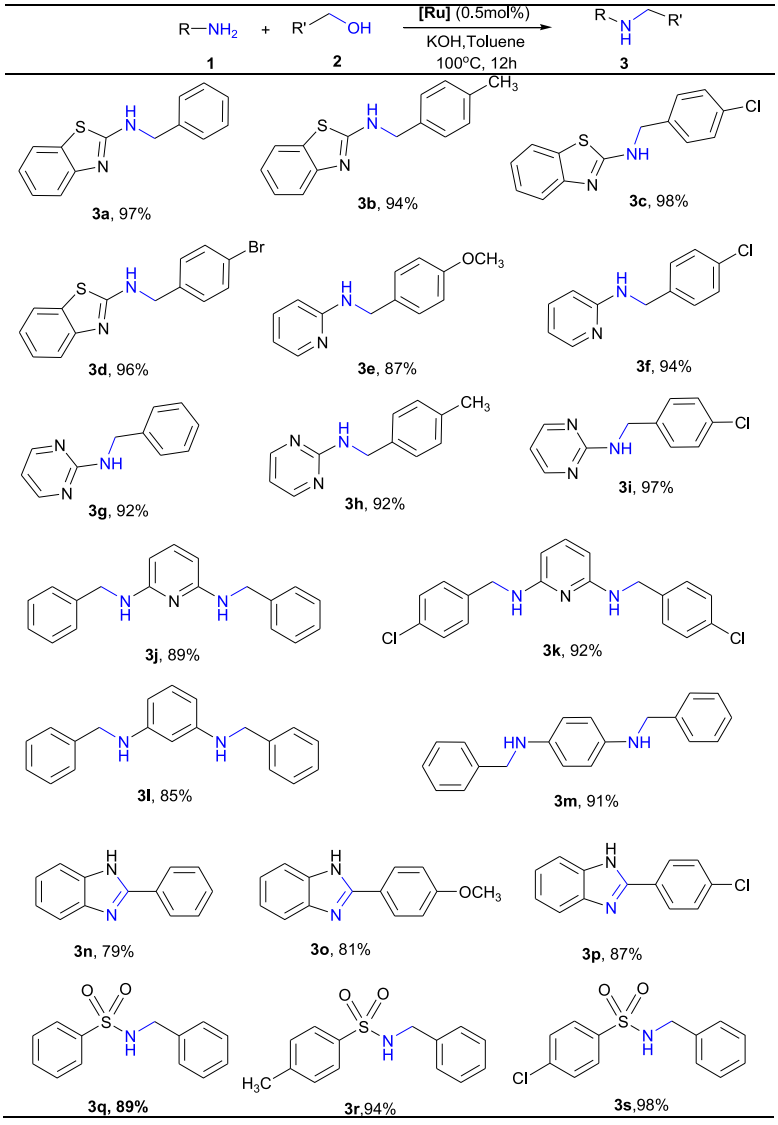
Table 5
Effect of substitution and catalyst loading on *N*-alkylation of 2-aminobenzothiazole with benzyl alcohol.[a]



Entry	Catalyst	Amount of catalyst (mol%)	Time (h)	TON[b]	Yield(%)[c]
1	**1**	1.0	12	94	94
2	**1**	0.5	12	186	93
3	**1**	0.3	24	287	86
4	**1**	0.2	24	370	74
5	**2**	0.5	12	180	90
6	**3**	0.5	12	178	89
7	**4**	0.5	12	196	97
8	**5**	0.5	12	192	96

[a] Reactions were carried out at 100 °C for 12 h using 2-aminobenzothiazole (1 mmol), $PhCH_2OH$ (1 mmol), catalyst, and base (50 mol %) in toluene (2 mL).
[b] Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.
[c] Isolated yields.

Table 6
N-Alkylation of various amines with alcohols.[a,b,c]



[a]Reactions were carried out at 100 °C for 12 h using amines (1 mmol), $PhCH_2OH$ (1 mmol), catalyst, and base (50 mol %) in toluene (2 mL). [b]Isolated yields. [c]Diamines (benzyl alcohol (2 mmol), diamines (1 mmol), catalyst **4** (0.10 mol %) were used.

N(1) = 86.5(3)°, C(1)–Ru(1)–S(1) = 89.0(3)°, N(1)–Ru(1)–S(1) = 81.49(6)°, N(1)–Ru(1)–Cl(1) = 86.87(8)° and S(1)–Ru(1)–As(1) = 88.61(18)° are more acute than 90°, whereas the other *cis* angles C(1)–Ru(1)–P(1) 90.2(3)°, N(1)–Ru(1)–P(1) = 91.45(5)°, C(1)–Ru(1)–As(1) = 96.4(3)° and P(1)–Ru(1)–As(1) = 98.46(16)°, are more obtuse than 90°. The *trans* angles P(1)–Ru(1)–S(1) = 172.92(2)°, C(1)–Ru–Cl(1) = 172.7(3)° and N(1)–Ru(1)–As(1) = 169.63(5)° deviate from linearity. The variations in bond lengths and angles lead to a significant distortion from an ideal octahedral geometry for the complex.

3.2. Catalytic studies

Ruthenium catalyzed *N*-alkylation using alcohol as an alkyl source has become an efficient method in organic synthesis as illustrated by several useful applications reported in the recent years [39]. The reaction conditions for this important process are relatively mild and environment friendly. The complexes **1**–**5** catalyzed the alkylation of heteroaromatic amines to the corresponding *N*-alkylated products via hydrogen autotransfer processes with KOH as the promoter. At the start of our studies, we investigated the *N*-alkylation of 2-aminobenzothiazole with benzyl alcohol in the presence of various bases, and the results have been summarized in Table 3. The catalytic reaction did not proceed well in the absence of a base or in the presence of weak bases (Entries 1–4). This is probably because the formation of $PhCH_2O^-$ ion is essential for the displacement of the Cl ligand in **1** to form the (benzyloxy)ruthenium species as a key intermediate. Thus, the

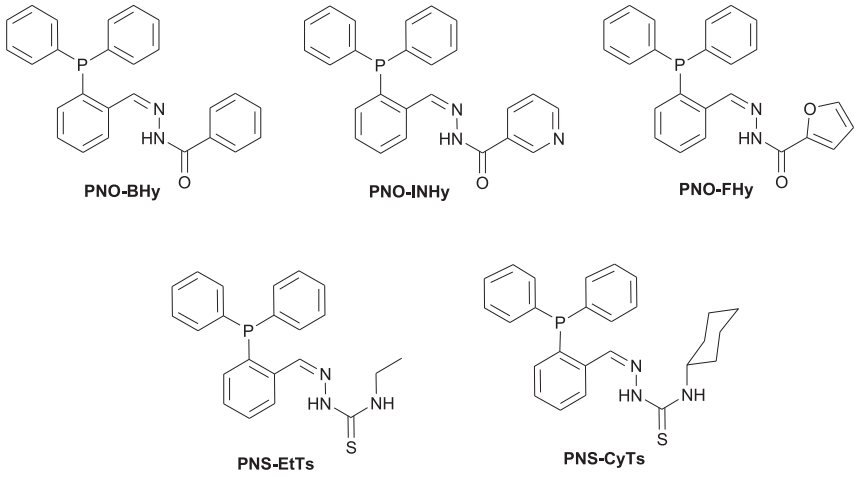
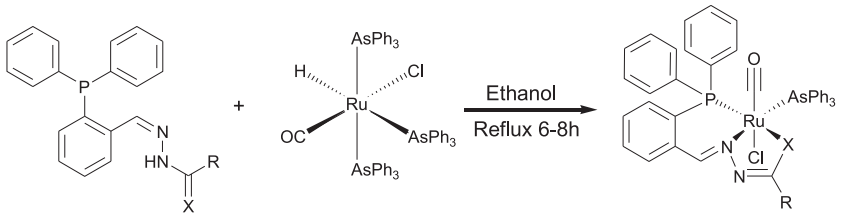


Fig. 2. Structure of the ligands designated by hydrazone and thiosemicarbazone used in this work.



R=-C_6H_5, X=O, (**PNO-BHy**)
R=-C_6H_4N, X=O, (**PNO-INHy**)
R=-C_5H_3O, X=O, (**PNO-FHy**)
R=-$NH(CH_3)$, X=S, (**PNS-EtTs**)
R=-$NH(C_5H_{11})$, X=S, (**PNS-CyTs**)

R=-C_6H_5, X=O, (**1**)
R=-C_6H_4N, X=O, (**2**)
R=-C_5H_3O, X=O, (**3**)
R=-$NH(CH_3)$, X=S, (**4**)
R=-$NH(C_5H_{11})$, X=S, (**5**)

Scheme 2. Synthetic strategy for the preparation of Ru(II) complexes with hydrazone/thiosemicarbazone ligands.

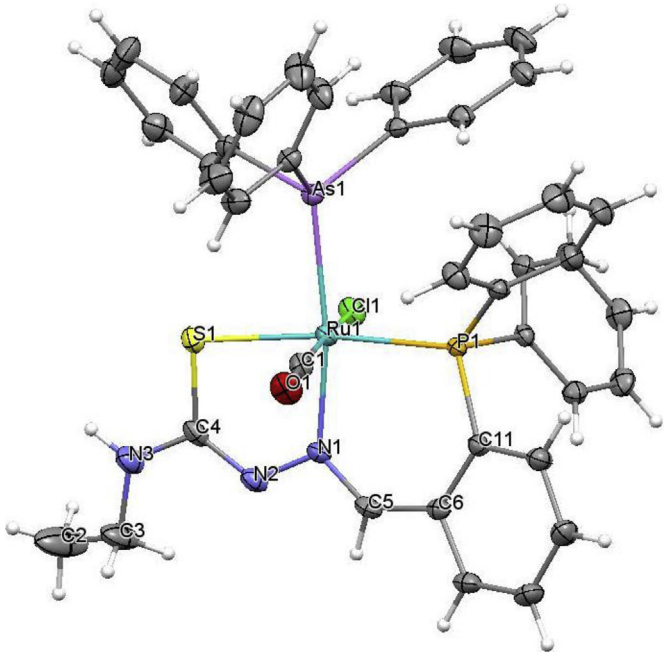


Fig. 3. Molecular structure of [(PNS–Et)RuCl(CO)($AsPh_3$)] (**4**). Ellipsoids are shown at the 35% probability level. The disordered chloride and carbonyl ligand of the structure have been omitted for clarity.

catalytic reaction successfully proceeded in the presence of strong bases (Entries 5–10), and benzothiozol-2-yl-benzylamine was obtained in 96% yield in the presence of a catalytic amount of KOH (50 mol %) (Entry 9).

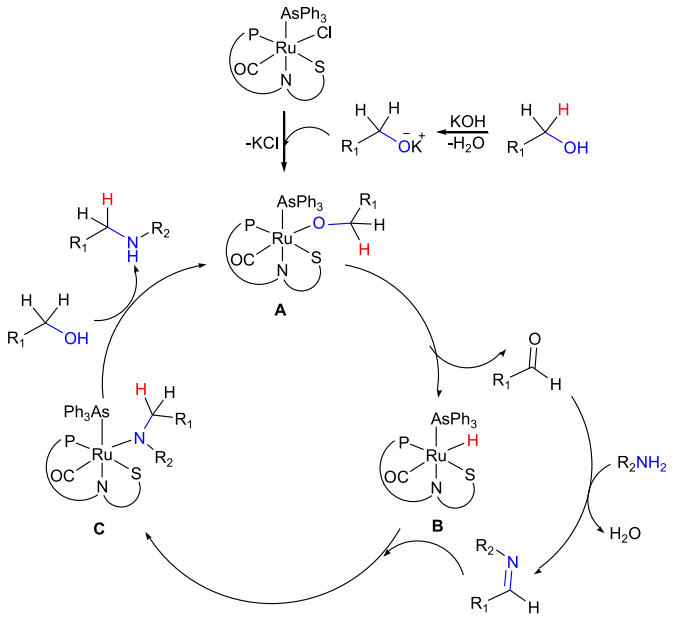
The reaction conditions were further optimized through different solvents and the results have been given in Table 4. Toluene was found as the best solvent for the *N*-alkylation reaction (Entry 5). No reaction occurred in the case of DMSO as solvent (Entry 6), while, DMF, ethanol, acetonitrile, benzene and THF resulted in much lower yields (Entries 1–4 and 7).

We continued the *N*-alkylation reaction optimization process after finding the need for a strong base to activate the ruthenium complex **1**. The following step was performed to study the influence of the substituents and catalyst loadings on the catalytic activity of ruthenium complexes (**1**–**6**). The results have been exhibited in Table 5 which indicate that lower catalyst loadings lead to moderate yields and longer reaction times are required to achieve maximum TONs (Entries 1–8). Also, as expected, higher catalyst loadings led to higher yields and higher amine content in the product distribution (Entries 1–8). Furthermore, considering the results when 0.5 mol % of catalyst was used, it is clear that ruthenium complexes containing ethyl group (Entry 7) as a terminal substituent led to higher yields than those containing phenyl/pyridyl/furyl or cyclohexyl (Entries 2, 5, 6, 7 and 8) and significantly shorter reaction times were needed to complete the *N*-alkylation process. This behavior reveals that the steric and electronic effects play an important role in terms of catalyst efficiency or in terms of generation of the catalytically active species. The results indicate

that the catalyst **4** is the most efficient catalyst among all, because of the presence of the least bulky moiety (+I effect), which appears to lead an improved activity. It is further inferred from the results that the sulfur containing thiosemicarbazone ligand (**PNS-EtTs**) in catalyst **4** may also influence the catalytic efficiency by their higher electronegativity nature.

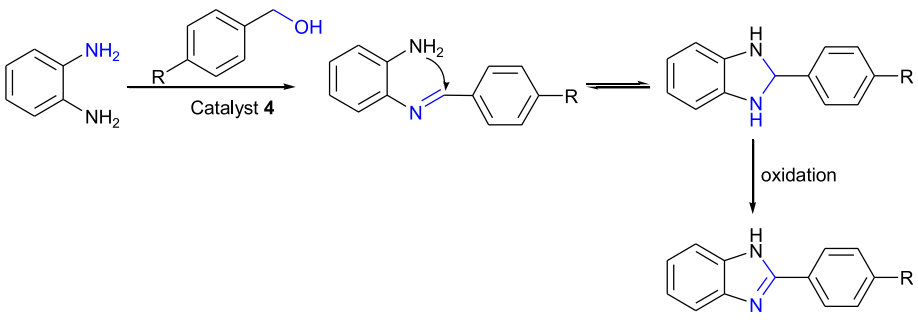
3.3. Substrate scope

After establishing the optimized reaction conditions, we investigated the substrate scope for this methodology. On the basis of results obtained, the complex **4** shows relatively better catalytic activity among the five complexes. Hence, the complex **4** was selected as the model catalyst for the coupling of heteroaromatic amines and diamines with substituted benzyl alcohols to afford the corresponding secondary amines; the results have been given in Table 6. When an equimolar solution of benzyl alcohol and 2-aminobenzothiazole with 0.5 mol % of catalyst **4** in toluene was used, the reaction went smoothly to afford the expected benzothiozol-2-yl-benzylamine (**3a**) in excellent isolated yield (97%). The reaction of 4-methylbenzyl alcohol with 2-aminobenzothiazole gave **3b** in 94% isolated yield. Another two new coupling partners, namely, 4-chlorobenzyl alcohol and 4-bromobenzyl alcohol, also furnished the corresponding secondary amines in 98% (**3c**) and 96% (**3d**) yields when combined with 2-aminobenzothiazole. Further substrate scope was examined under identical conditions when 4-methoxybenzyl alcohol and 4-chlorobenzyl alcohol successfully furnished respective *N*-alkylated products with 2-aminopyridine in 87% (**3e**) and 94% (**3f**) yields. Similarly, the coupling of benzyl alcohol and 2-aminopyrimidine yielded *N*-benzylpyrimidin-2-amine (**3g**) in 92% isolated yield. Both electron-donating and electron-withdrawing 4-methylbenzyl alcohol and 4-chlorobenzyl alcohol were converted into the corresponding amines in good isolated yields of 92 and 97% (**3h** and **3i**), respectively. One of the outstanding properties of the present catalyst is its high selectivity for monoalkylation of heteroaromatic amines. Hence, it was of interest to determine whether this selectivity for the monoalkylation of primary aromatic functions could be used for the *N,N'*-dialkylation of diamines. Primarily, 2,6-diaminopyridine was reacted with benzyl alcohol, which afforded *N,N'*-dialkylated product (**3j**) with 89% yield. The *N,N'*-dialkylation with benzyl alcohols bearing a halogen atom (-Cl) proceeded to give the corresponding product **3k** with excellent yield 92%. Encouraged by the promising results, we further looked at extending the above methods to other diamines and alcohols. The dialkylation of *m*-phenylenediamines was successfully carried out with benzylic alcohol in 85% (**3l**) yield. Similar to *m*-phenylenediamines, *p*-phenylenediamines also reacted with benzyl alcohol smoothly to give the corresponding product **3m** (91%) in excellent yields. Instead of *N,N'*-dilkylation, reaction of *o*-phenylenediamine with benzyl alcohol gave 2-phenyl-1H-benzo[d]imidazole (**3n**) as the exclusive product (79%) under the catalytic conditions described for other alkylations. Reaction of *o*-phenylenediamine with 4-chlorobenzyl alcohol afforded the desired 2-substituted benzimidazole in 81% (**3o**) isolated yield. 4-Methoxybenzyl alcohol could also be alkylated, revealing the formation of solely 2-(4-methoxyphenyl)-1H-benzimidazole (**3p**) in 87% yield after 12 h of reaction time. The formation of 2-arylbenzimidazole product is due to the *N*-alkylation of *o*-phenylenediamine to corresponding imines, followed by *in-situ* cyclization and oxidation (Scheme 3). The formation of cyclized product is due to the intramolecular attack of an amino group at the imine functionality (Scheme 3). *N*-Alkylated sulfonamide derivatives are pharmaceutically active compounds and a difficult class of substrate and remain as an essential research topic in organic synthesis. The compatibility of the catalytic system with sulfonamide was demonstrated, and very good results (**3q**) were obtained for the coupling of sulfonamide with benzyl alcohols using the catalyst **4**. Thus, reaction of 4-methylbenzenesulfonamide and 4-chlorobenzenesulfonamide with benzyl alcohol gave the corresponding amides and were isolated in 94 and 98% yields (**3r** and **3s**), respectively.



Scheme 4. Plausible mechanism for *N*-alkylation.

A possible catalytic cycle is proposed in Scheme 4 on the basis of the results obtained and available literature on similar rutheniumcatalyzed transformations [40]. This catalysis is considered to proceed via the (benzyloxy)ruthenium intermediate **A**, which



Scheme 3. *N*-alkylation of *o*-phenylendiamine and *in-situ* cyclization to 2-arylbenzimidazole.

undergoes β-hydrogen elimination to give the ruthenium hydride **B** 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 **B**, followed by alcoholysis of the resulting (amido)ruthenium species **C**, affords $R_1CH_2NHR_2$ as the *N*-alkylation product and reproduces the (benzyloxy)ruthenium intermediate **A** and completes the catalytic cycle. The effective formation of the intermediates **C** may depend on the steric and electronic properties of the imine or iminium ion. In comparison with previously reported ruthenium(II) complexes bearing chelating tridentate phosphine ligands [16–26], our catalytic system led to better yields and lower catalyst loadings were needed to complete the *N*-alkylation of a wide range of heteroaromatic amines, diamines and sulfonamides. Also, the catalyst **4** have proven to be an alternative for the selective synthesis of 2-alkyl substituted benzimidazoles, which are key intermediates for the manufacture of commercially important compounds such as agrochemicals, dyes, and medicines [41].

4. Conclusions

We have reported the synthesis and characterization of a series of ruthenium(II) carbonyl complexes bearing phosphine-functionalized hydrazone/thiosemicarbazone ligands and triphenylarsine co-ligands. Typically, [(**PNO-BHy**)RuCl(CO)($AsPh_3$)], [(**PNO-NHy**)RuCl(CO)($AsPh_3$)], [(**PNO-FHy**)RuCl(CO)($AsPh_3$)], [(**PNS-EtTs**)RuCl(CO)($AsPh_3$)] and [(**PNS-CyTs**)RuCl(CO)($AsPh_3$)] were synthesized by reactions of [RuHCl(CO)($AsPh_3$)$_3$] precursors with deprotonated diphenylphosphino-hydrazone/thiosemicarbazone ligands. The structures of these complexes were unambiguously determined by analytical, spectroscopic and single crystal X-ray diffraction methods (for complex **4**). The catalytic study of complexes **1**–**5** towards amine *N*-alkylation reactions was completed, showing that all catalysts are active toward catalytic transformations. The results also showed that steric and electronic effects of the ligands play a more important role in the catalytic activity of the new complexes. In the *N*-alkylation process the complex **4** has been proven to be versatile and an efficient catalyst under moderate conditions in comparison to its analogs and other ruthenium and iridium complexes [42]. Also, the complex **4** has shown high tolerance to functional groups in the amine and alcohol moieties. These results demonstrate the high versatility and application potential of phosphine-functionalized hydrazone/thiosemicarbazone ligands in the design of effective homogeneous catalysts.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.05.054.

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