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**Efficient and Versatile Catalysis of *N*-alkylation of Heterocyclic Amines with Alcohols and One-pot Synthesis of 2-aryl Substituted Benzazoles with Newly Designed Ruthenium(II) Complexes of PNS Thiosemicarbazones**

**Rangasamy Ramachandran,<sup>a</sup> Govindan Prakash<sup>a</sup>, Sellappan Selvamurugan<sup>a</sup>, Periasamy Viswanathamurthi,<sup>\*a</sup> Jan Grzegorz Malecki,<sup>b</sup> Venkatachalam Ramkumar<sup>c</sup>**

<sup>a</sup>*Department of Chemistry, Periyar University, Salem-636 011, India.*

<sup>b</sup>*Department of Crystallography, Silsian University, Szkolna 9, 40-006 Katowice, Poland*

<sup>c</sup>*Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India*

\*To whom correspondence should be made, e-mail: [viswanathamurthi72@gmail.com](mailto:viswanathamurthi72@gmail.com);

*Fax: +91 427 2345124*

**Abstract:**

Ruthenium(II) carbonyl complexes with phosphine-functionalized **PNS** type thiosemicarbazone ligands [RuCl(CO)(EPh<sub>3</sub>)(L)] (**1-6**) (E = P or As, L = 2-(2-(diphenylphosphino)benzylidene)thiosemicarbazone (**PNS-H**), 2-(2-(diphenylphosphino)benzylidene)-*N*-methylthiosemicarbazone (**PNS-Me**), 2-(2-(diphenylphosphino)benzylidene)-*N*-phenylthiosemicarbazone (**PNS-Ph**)) have been synthesized and characterized by elemental analysis and spectroscopy (IR, UV-Vis, <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P-NMR) as well as ESI mass spectrometry. The molecular structure of complexes **1**, **2** and **6** were identified by means of single-crystal X-ray diffraction analysis. The analysis revealed that all the complexes possess a distorted octahedral geometry with the ligand coordinating through uni-negative tridentate **PNS** fashion. All the ruthenium complexes (**1-6**) were tested as catalyst for *N*-alkylation of hetero aromatic amines with alcohols. Notably, the complex **2** was found to be very efficient and versatile catalyst towards *N*-alkylation of wide range of heterocyclic amines with alcohols. The complex **2** can also catalyze the direct amination of 2-nitropyridine with benzyl alcohol to the corresponding secondary amine. Furthermore, a preliminary examination of performance for *N,N*-dialkylation of diamine showed promising results, giving good conversion and high selectivity. In addition *N*-alkylation of *ortho*-substituted anilines (-NH<sub>2</sub>, -OH and -SH) led to the synthesis of 2-aryl substituted benzimidazoles, benzoxazoles and benzothiazoles in one-pot also revealed the catalytic activity of the complex **2**.

**Key words:** PNS Thiosemicarbazone ligands, Ruthenium(II) complexes, X-ray diffraction, *N*-alkylation, One-pot synthesis of benzazoles

## Introduction

The nature of the multidentate ligand has a profound effect on the coordination chemistry of a metal complex, and so design and “tailoring” of ligand properties can lead to innovative metal chemistry<sup>1</sup>. Special interest has been directed to the use of multidentate thiosemicarbazone ligands having both hard and soft donor atoms (e.g. N<sub>2</sub>S<sub>2</sub> or XNS, X=N, O, S and P), because of their coordination versatility<sup>2</sup> and remarkable applications in catalytic<sup>3</sup> and biological sciences.<sup>4</sup> 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.<sup>5</sup>

Several donor groups have been reported to functionalize thiosemicarbazones, their complexes exhibit high activity when used as catalyst in Pd-catalyzed Suzuki–Miyaura cross coupling,<sup>6</sup> Heck or Buchwald-Hartwig amination reactions.<sup>7</sup> More recently, ruthenium mediated *N*-alkylation and transfer hydrogenations have also appeared in the literature.<sup>8</sup> We have a continuing broad interest in thiosemicarbazone ligand systems containing diphenylphosphino pendant functionalities that can potentially form stable complexes with metal ions. Since the first synthesis, performed by Brceski and co-workers,<sup>9</sup> phosphino-thiosemicarbazone ligands have been widely used in catalysis. With the simultaneous presence of soft P, S and hard N donors, the phosphino-thiosemicarbazone ligands exhibit various coordination modes (Scheme 1): (a) neutral tridentate (P, N and S bonded to M),<sup>10</sup> (b) monoanionic tridentate (P, N and deprotonated S bonded to M),<sup>11</sup> (c) neutral bidentate (P and S bonded to M)<sup>12</sup> and (d) monoanionic bridging ligand (P bonded to M and S bonded to M').<sup>13</sup> Coordination through neutral bidentate and monoanionic bridging PNS ligands are found in some Au(I) and Ag(I) complexes.<sup>13,14</sup> It has been suggested that intramolecular hydrogen bonding exists between the terminal thioamide nitrogen atoms as donors and the imine nitrogen atoms as acceptors. The PNS ligands, which do not form an intramolecular hydrogen bond, tend to coordinate predominately in a neutral or monoanionic tridentate PNS fashion. Examples for this type of coordination is rare and so far only known for complexes with Cu(I) and Au(II).<sup>11,15</sup> This variable mode of binding of phosphino-thiosemicarbazone has encouraged us to explore its coordination chemistry further, and herein we have chosen ruthenium as the metal center to interact with the thiosemicarbazone.

One reason behind the choice of this particular metal center is its ability to take up different coordination environments with salicylaldehyde/naphthaldehyde thiosemicarbazones, have been reported recently,<sup>16</sup> which makes its coordination chemistry very interesting.

Amines are key building blocks in industrial and medicinal chemistry today.<sup>17</sup> Traditionally, these compounds are synthesized by alkylation of primary amines with good leaving groups such as alkyl halides, tosylates, mesylates and triflates.<sup>18</sup> However, the procedure frequently leads to over alkylation and, considering the necessity for environmentally friendly processes, the high toxicity of many alkylating agents is a major drawback, especially in pharmaceutical, biochemical and industrial applications. Nevertheless, the use of transition metal complexes as catalysts via a borrowing-hydrogen methodology makes the *N*-alkylation using alcohols a potentially less hazardous and more atom-economical process.<sup>19-24</sup> While both heterogeneous and homogeneous catalysts have been known to promote the reaction,<sup>19b</sup> iridium<sup>20</sup> and ruthenium<sup>21-23</sup> complexes have constituted a vast majority of the homogeneous catalysts because of their high catalytic performance with high product selectivity. Several iridium and ruthenium catalytic systems bearing phosphine ligands have been reported to complete the *N*-alkylation of amines with alcohols with good yields and selectivity.<sup>24</sup>

Pyrimidine, ferrocene and sulfonamide are currently considered as privileged scaffolds and have gained remarkable popularity in the fields of bioorganic and medicinal chemistry.<sup>25</sup> In particular, 2-(*N*-alkylamino)pyrimidines, 2-(*N*-alkylamino)ferrocene and 2-(*N*-alkylamino)sulfonamides exhibit a wide range of biological properties. Selective examples are *N*-methyl-D-aspartate receptor antagonists, ferroquine and histone deacetylase inhibitors.<sup>26</sup> Bioactive molecules possessing the 2-(*N*-alkylamino)benzothiazole core such as R116010 (II), a potent inhibitor of retinoic acid metabolism, riluzole (I), a glutamate neurotransmitter and *N*-myristoyltransferase (Nmr) inhibitor.<sup>27</sup> In addition, benzazole such as benzimidazoles, benzoxazole and benzothiazoles are important structural motifs in pharmaceuticals,<sup>28</sup> which involve nearly one-quarter of the top-100 selling drugs including DF203, ERB-O41 and omeprazole (Scheme 2).<sup>29</sup> Development of general methods for the synthesis of these heterocyclic compounds is thus highly relevant for drug discovery.

In view of the above and as a part of our ongoing research work,<sup>8a,16a,30</sup> we report herein a series of ruthenium(II) carbonyl complexes bearing phosphino-thiosemicarbazone ligands and

investigate the role of terminal substitution of ligands and co-ligands in determining catalytic activity for *N*-alkylation of amines and one-pot synthesis of 2-aryl substituted benzimidazoles, benzoxazoles and benzothiazoles. The attractive features of these reactions include the use of low toxic organic materials, excellent atom economy, water is the only byproduct and high selectivity towards the products.

## Results and discussion

### Catalyst design

In designing Ru complexes (**1–6**) (Scheme 3), we were interested in probing the role of catalysis of terminal *N*-substitution in phosphino-thiosemicarbazones (**PNS-H**, **PNS-Me** and **PNS-Ph**), co-ligands, and resulting differences in the structure of the complexes (**1–6**). The ruthenium(II) complexes (**1–6**) are closely related, only differing by H versus Me or Ph in the terminal *N*-substituent and P or As in coligands. The ligand precursors **PNS-H**, **PNS-Me** and **PNS-Ph** (Scheme 3) were synthesized by condensation of 2-diphenylphosphinebenzaldehyde with thiosemicarbazide, 4-*N*-methylthiosemicarbazide and 4-*N*-phenylthiosemicarbazide respectively, following the published procedure.<sup>9–15</sup> The new Ru catalyst of the type [RuCl(CO)(EPh<sub>3</sub>)(L)] (**1–6**) were synthesized by reacting **PNS-H**, **PNS-Me** and **PNS-Ph** with one equivalent of [RuHCl(CO)(EPh<sub>3</sub>)<sub>3</sub>] in ethanol under reflux for 6–8 h (see Scheme 3 for further details). These Ru complexes are air stable, were obtained in good yield (73–82%), and were characterized by analytical, spectroscopic methods (IR, UV-Vis, <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P-NMR and ESI-MS) (Fig. S1–S30, ESI†) and by X-ray crystallography for **1**, **2** and **6** as described further below. The analytical data of the complexes agreed well with the proposed molecular formulae.

### Spectroscopic Studies

The IR spectra of the ligands and the corresponding ruthenium(II) complexes provided significant information about the metal ligand bonding. A strong vibration observed at 1546–1541 cm<sup>-1</sup> in the ligands corresponding to  $\nu_{C=N}$  was shifted to 1592–1582 cm<sup>-1</sup> in all the complexes indicating the participation of azomethine nitrogen in bonding.<sup>15</sup> A sharp band observed at 760–758 cm<sup>-1</sup>, ascribed to  $\nu_{C=S}$  in the ligands, has completely disappeared in the spectra of all the new Ru complexes and the appearance of a new band at 747–738 cm<sup>-1</sup> due to  $\nu_{C-S}$  indicated the coordination of the sulfur atom after enolisation followed by deprotonation.<sup>16a</sup>

All the complexes display a medium to strong band in the region 1962–1945  $\text{cm}^{-1}$ , which is attributed to the terminally coordinated carbonyl group ( $\text{C}\equiv\text{O}$ ) and is observed at a slightly higher frequency than in the precursor complexes.<sup>16b</sup> In addition, vibrations corresponding to the presence of  $\text{PPh}_3/\text{AsPh}_3$  also appeared in the expected region. The electronic spectra of the complexes (**1–6**) have been recorded in dichloromethane and they displayed four bands in the region around 231–435 nm. The high-energy absorption shoulder in the region 231–258 nm have been assigned to ligand-centered (LC) transitions,<sup>31</sup> the lowest energy shoulder observed in the region 343–369 nm have been attributed to the ligand to metal charge transfer (LMCT) transitions, and the bands 427–435 nm has been assigned to a forbidden ( $d\rightarrow d$ ) transition.

The  $^1\text{H}$  NMR spectra of the ligands and their complexes (**1–6**) show the signals in the expected regions (Fig. S1–S9, ESI†). The singlets that appeared for the  $\text{N-NH-C=S}$  proton of the free ligands at 11.94–11.52 ppm are absent in the complexes, supporting the enolization and coordination of the thiolate sulphur to the  $\text{Ru(II)}$  ion. The doublet due to azomethine proton (8.86–8.73 ppm) in the complexes are slightly downfield compared to the free ligands (8.79–8.65 ppm), suggesting deshielding upon coordination to  $\text{Ru(II)}$  ion. The spectra of the complexes showed a singlet at 8.60–8.15 ppm, which has been assigned to  $\text{NH}_2$  or  $\text{NH-R}$  protons. Further, the spectra of all the complexes showed a series of signals for aromatic protons at 7.88–6.51 ppm. In addition, a singlet appeared around 1.22 ppm for complexes **2** and **5** corresponding to the terminal  $-\text{CH}_3$  group protons.

The  $^{13}\text{C}$  NMR spectra show the expected signals in the appropriate regions (Fig. S10–S18, ESI†). For the uncoordinated ligands, the  $\text{C=N}$  and  $\text{C=S}$  signals appear in the regions around 141.50–140.64 ppm and 178.93–175.81 ppm. Upon coordination and formation of the new  $\text{Ru}$  complexes, a downfield shift is observed for the signals of the  $\text{C=N}$  (around 5 ppm), while the  $\text{C=S}$  carbon atom signals are appeared in the upfield region between 176.45 and 176.03 ppm. This is consistent with the P, N, S coordination and thioenolization of the  $\text{C=S}$  of thiosemicarbazone moieties. In complexes (**1–6**), aromatic carbon atoms of the phenyl group observed around 138.91–115.83 ppm are comparable to the literature values.<sup>32</sup> The  $\text{C}\equiv\text{O}$  carbon resonating at 206.73–206.02 ppm is comparable with earlier observations.<sup>33</sup> In addition, a signal appeared around 31.17–30.60 ppm for complexes **2** and **5** corresponding to the terminal methyl group carbon.

The presence of a residual PPh<sub>3</sub> coordinated to Ru(II) (**1–3**) is confirmed by <sup>31</sup>P NMR (Fig. S19–S24, ESI†), where two doublets are observed respectively at 30.15–29.79 ppm ( $J_{pp} = 22.6$  Hz, PPh<sub>3</sub>) and 28.85–28.74 ppm ( $J_{pp} = 24.2$  Hz, PPh<sub>2</sub>). These values for coupling constants suggest a *cis* disposition between the phosphorus nuclei, as already reported for other Ru(II) phosphine complexes.<sup>34</sup> The singlet observed at 32.73–31.38 ppm in complexes **4**, **5** and **6**, respectively, suggested the presence of PPh<sub>2</sub> group in the thiosemicarbazone moieties. ESI-mass spectra for the complexes (**1–6**) generally show the molecular ion peak with the loss of a chloride ion (Fig. S25–S30, ESI†).

### Structural studies

Even though the analytical and spectral data gave some idea about the molecular formulae of the complexes, they do not indicate the exact coordination of phosphino-thiosemicarbazone units in them. Hence, there is a need to prove their structures by X-ray crystallography. The crystal data and structure refinement parameters for complexes **1**, **2** and **6** are summarized in Table 1 and selected bond lengths and bond angles are depicted in Tables 2. The ORTEP view of the complexes **1**, **2** and **6** along with the atomic numbering scheme are given in Figures 1–3. The single-crystal X-ray studies revealed that complexes **1** and **2** are crystallized in a monoclinic system with the space group  $P2_1/c$ , whereas complex **6** crystallized in a triclinic system with the space group  $P\bar{1}$ . The coordination geometry around the Ru(II) ion is a slightly distorted octahedron, where the basal plane is constructed of phosphorus atom, the imine nitrogen and the thiolate sulfur atom of the ligand in its mononegative tridentate PNS fashion, and a triphenylphosphine/triphenylarsine. The remaining apical coordination sites are filled up by a chlorine atom and carbonyl group. The chloride and carbonyl ligands of the complexes **1** and **2** are disordered in two orientations with ratio 51:49 for **1** and 55:45 for **2**, respectively.<sup>35a,b</sup> In the complexes **1**, **2** and **6** the coordination sphere is same and the general structural motifs differ only in the terminal substitution ( $R = H, Me, Ph$ ). Thus the structure of one of the Ru(II) complex **1** (Figure 1) will be described in detail here.

The tridentate PNS chelate ligand coordinated equatorially to the metal ion with the formation of one six-membered ring and another five membered ring with the bite angles of 90.63(7) [N(1)–Ru(1)–P(1)] and 81.21(7) [N(1)–Ru(1)–S(1)]. This results in a significant distortion of the {RuP<sub>2</sub>NS(CO)Cl} core from the ideal octahedral geometry, which is reflected in the twelve *cis*



and three *trans* angles. As expected, the PPh<sub>3</sub> ligand occupies mutually *cis* position to PPh<sub>2</sub> head in the thiosemicarbazone chain for better  $\pi$  interaction.<sup>35b</sup> 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 molecules. The equatorial bond lengths are 2.127(11) [Ru(1)–N(1)] Å, 2.125(3) Å [Ru(1)–P(2)], 2.3859(8) [Ru(1)–S(1)]Å and Ru(1)–P(2) = 2.3982(8) Å. For complexes bearing P, N–iminophosphine ligands, the higher *trans* influence of the phosphorus atom in comparison to that of the imine donor functionality leads to longer distances for bonds *trans* to the phosphorus.<sup>36</sup> On the other hand, in the presence of tridentate P,N,S ligands (with N being an iminic nitrogen) the reverse situation is usually observed,<sup>15</sup> the related bond distances in [RuCl(CO)(PPh<sub>3</sub>)(PNS-H)] (namely, Ru(1)–N(1) = 2.125(3) Å, Ru(1)–P(2) = 2.3982(8)) follow this rule. The other two axial sites are occupied by a carbonyl group and one chlorine ligand with Ru(1)–C(1A) and Ru(1)–Cl(1) distance of 1.88(2) Å and 2.441(4) Å. The CO group occupies the site *trans* to the Cl (N(1)–Ru1–P(2) = 169.37(7)). This may be a consequence of strong Ru<sup>II</sup>→CO back donation as indicated by the short Ru–C [1.88(2) Å] bond and low CO stretching frequency (1949 cm<sup>-1</sup>), which prefers  $\sigma$  or  $\pi$  weak donor groups occupying the site opposite to CO to favor the d– $\pi$  back donation.

After a careful literature search concerning ruthenium complexes derived from thiosemicarbazone ligands, we have found several examples of ruthenium complexes with XNS (O, N, C) thiosemicarbazone ligand type.<sup>8b,16,37</sup> Nevertheless, the number of complexes containing Ru PNS thiosemicarbazone is still scarce. Having this fact into account, we must stress the novelty of the ruthenium(II) complexes (**1–6**) reported in this article, because it is the first example of phosphine-functionalized thiosemicarbazone ruthenium(II) complexes.

## Catalytic Studies

### Optimization for *N*-alkylation reaction conditions

To investigate a promising catalytic system, a screen was performed for a model reaction between 2-aminopyridine and benzyl alcohol. The representative results are shown in Table 3. In the absence of base, *N*-alkylation of amine was not observed (entry 1). Weak bases such as K<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> were ineffective (entries 1–2 and 14). The reaction was considerably accelerated by the addition of a strong base (entries 5–13). When the reaction was carried out in

the presence of KOH, *N*-benzylaminopyridine was formed in an excellent yield (upto 99%), which we considered to be the choice of the base (entry 5–8). Other strong bases, such as KO*t*Bu and NaOH were also found effective (entries 9–12 and 13). In addition, to obtain almost quantitative yields and avoid the presence of the imine as a secondary product, from lack of hydrogenation of the condensation product, at least 2 equivalent of base with respect to substrate is needed.

The ability to use small amounts of catalyst and still achieve high conversions is a great concern in *N*-alkylation reactions due to the high cost of metals and ligands used. 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 to study the influence of the terminal substituents, coligands and catalyst loadings on the catalytic activity. The results are summarized in Table 4. The blank experiment was carried out without catalyst, and no product formation is observed in these conditions, which excluded the contribution of base itself as a catalyst (entry 1). The results indicate that lower catalyst loadings lead to moderate yields and longer reaction times are required to achieve maximum conversion (entries 2–13). Also, as expected, higher catalyst loadings led to higher yields and higher amine content in the product distribution (entries 14–19). Furthermore, considering the results when 0.5 mol % of catalyst was used, it is clear that ruthenium complexes containing methyl group (entry 15) as a terminal substituent lead to higher yields than those containing hydrogen or phenyl (entries 14 and 16) and significantly shorter reaction times are needed to complete the *N*-alkylation process. This behavior indicates that steric effects may also play an important role in terms of catalyst efficiency or in terms of the generation of the catalytically active species. In addition, complexes **1**, **3**, and **6** showed good activity at lower catalyst loadings, but when the catalyst concentration was increased, it was not possible to obtain yields as high as those with their analogues. However, it is important to note that, among complexes with methyl substituents in the terminal positions, those containing PPh<sub>3</sub> and AsPh<sub>3</sub> as coligands in **2** and **5**, showed the best selectivity toward the synthesis of the amine (entries 15 and 18). Thus, electronic properties may also account for the catalytic activity, although as much as steric effects.

We believe that the catalytic amine alkylation with ruthenium(II) complexes follows the ‘borrowed hydrogen’ pathway, extensively studied by Williams, Fujita, Yamaguchi and others.<sup>19-</sup>

<sup>27</sup> The alcohol is catalytically dehydrogenated to the corresponding aldehyde (*in-situ* oxidation) in the first step. Then, the aldehyde condenses with the amine to give an intermediate imine, which is subsequently hydrogenated (reduction) by the catalyst. Thus, there is no net H<sub>2</sub> consumption in this process, however, the reaction benefits from being run in a closed system preventing irreversible H<sub>2</sub> loss.

### ***N*-alkylation of heterocyclic amines and amides**

In order to check the versatility of our catalysts, we decided to study the substrate scope of the catalyst **2** with other amine/amide and alcohol derivatives. The results showed in Table 5 summarize the effect of the substrates on the yield and selectivity of the catalytic reaction, using a 0.5 mol % loading of catalyst in toluene at 100 °C. The reactions of 2-aminopyridine with benzyl alcohols bearing electron-donating and -withdrawing substituents at the aromatic ring proceeded smoothly to give the corresponding *N*-benzylaminopyridine in good to high yields (**1a–1e**). Benzyl alcohols with *p*-MeO, *p*-Cl and *p*-Br were tolerant (**1c–1e**). The reaction of sterically demanding 2-methylbenzyl alcohol also proceeded to give the corresponding amine in good yield (**1b**). Similar to the case of 2-aminopyridine, the *N*-alkylation of 2-aminopyrimidine with benzyl alcohol and *para*-methyl, -methoxy substituted benzyl alcohols, gave the corresponding products **2a–2c** with 97, 86 and 83% yields, respectively. The *N*-alkylation with benzyl alcohols bearing a halogen atom (Cl or Br) proceeded to give the corresponding products **2d** and **2e** with excellent yields as well. 2-aminobenzothiazole also reacted with benzylic alcohols to afford the desired products in 92, 81, 79, 97 and 94% respectively (**3a–3e**). Interestingly, the reaction of *p*-toluenesulfonamide with benzylic alcohols afforded the corresponding alkylated sulfonamide in good to excellent yields (76–99%; **4a–4e**). The present protocol also performed for *N*-alkylation of amines such as aminobenzene, 2-aminopyridine, 4-methyl, 4-chloro and 4-bromoaniline with ferrocenemethanol in high yield (**5a–5e**).

It is worth mentioning that complex **2** can also catalyze the direct amination of 2-nitropyridine with benzyl alcohol, which is more sustainable for the synthesis of amines.<sup>38</sup> Typically, a mixture of 2-nitropyridine, potassium hydroxide, catalyst **2** and benzyl alcohol was heated at 100 °C for 12 h, and *N*-benzylpyridine was obtained in 96% yield (scheme 4). Apparently, the reduction of a nitro group can be achieved by a hydrogen transfer reduction with **2**.

### ***N*-alkylation of hetero aromatic diamine**

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. Only very few synthetic procedures for the preparation of such compounds can be found in the literature.<sup>39</sup> In most cases, these transformations are either not selective or have to be performed in several steps and thus lack of general applicability towards a broad range of substrate.<sup>40</sup> As evident from the results in scheme 5, it is possible to selectively monoalkylated both amino functions of the diamine, affording the corresponding product (**6a–6f**) in excellent yields. First 2,6-diaminopyridine was reacted with benzyl alcohol, which afforded *N,N'*-dibenzylpyridine-2,6-diamine (87%; **6a**). Next, several substituted benzyl alcohols were employed, and, as determined before for the alkylation of heterocyclic amines (Table 5), both electron-donating and electron-withdrawing substituents in the *para* position are well-tolerated, these reactions affording the dialkylated products in yields ranging from 62 to 93% (**4a–4e**). Also, the reaction with ferrocenemethanol did not distress the yield of the corresponding dialkylated product (**6f**).

### ***N*-alkylation of *ortho*-substituted anilines: synthesis of benzimidazoles, benzothiazoles and benzoxazole**

The most commonly used methods for the synthesis of benzazoles include the condensation of *ortho*-substituted (–NH<sub>2</sub> or –SH or –OH) anilines with aldehydes,<sup>41</sup> nitriles,<sup>42</sup> carboxylic acids,<sup>43</sup> or acyl chlorides.<sup>44</sup> Most of these methods are associated with the limitations such as poor selectivity, side reactions, tedious work-up procedures and requirement of special oxidation process. Alternatively, few reports are also available on the synthesis of benzazoles directly from alcohols.<sup>45</sup> Recently, Ru/Xanthphos,<sup>46</sup> Ru,<sup>47</sup> IBX<sup>48</sup> have been applied for the synthesis of benzimidazole. Deng *et al.* reported dppf [1,1'-bis(diphenylphosphino)ferrocene] catalyzed synthesis of 2-arylbenzoxazoles directly from *o*-nitrophenols and benzyl alcohols.<sup>49</sup>

Although, the reaction conditions were similar as for the *N*-alkylation, however, reaction took longer time for completion at slightly higher temperatures. Various experiments were carried out to optimize the *N*-alkylation of *ortho*-substituted anilines (Table 6). In order to explore the scope

of the present method, the reactions of *o*-substituted ( $-\text{NH}_2$  or  $-\text{OH}$  or  $-\text{SH}$ ) anilines were successfully performed with a variety of alcohols (Table 7). The reaction of *o*-phenylenediamine was carried out with benzyl alcohol to obtain 2-phenylbenzimidazole (**7a**) in 93% yield. Functionalized alcohols, such as 4-methoxybenzyl alcohol and 4-chlorobenzyl alcohol were utilized to afford the corresponding products **7b** and **7c** in 81 and 98% yields, respectively. Heterocyclic alcohol, 2-pyridylmethanol, gave the corresponding product (**7d**) in high yield. However, low yield was obtained with aliphatic alcohol, isoamyl alcohol (**7e**). The reaction of 2-aminophenol with benzyl alcohol and benzyl alcohols bearing an electron-donating group and an electron-withdrawing group afforded the corresponding products **7f–7i** with 84–99% yields respectively. In addition heteroaromatic alcohol gave the corresponding benzothiazole product in high yield. Reaction of aminothiophenol with benzyl alcohol and 4-substituted benzyl alcohols afforded the desired 2-aryl substituted benzoxazoles in excellent yields. In the case of benzyl alcohol (93%, **7k**), 4-methoxybenzyl alcohol (81%, **7l**) and 4-chlorobenzyl alcohol (96%, **7m**) good to excellent yields were observed. The reaction was also applied to 2-pyridylmethanol, but the desired products obtained in low yield.

A possible mechanism to rationalize this transformation is illustrated in Scheme 6. Starting from alcohol, catalytic hydrogen transfer to an appropriate  $\text{H}_2$  acceptor (Ru catalyst) via “Oxidation 1” would lead to the formation of aldehyde **A**. Condensation of **A** with *ortho*-substituted anilines generates an intermediate imine **B**, which can be in equilibrium with dihydrobenzazole **C**. A second hydrogen-transfer process from **C** then provides a route to benzazole **D** via “Oxidation 2” with Ruthenium(II) catalyst. To confirm this, controlled experiments were carried out with and without ruthenium catalyst (entries 1 and 5 respectively, Table 6). The yield of desired product decreased drastically without ruthenium catalyst. On the other hand reaction of *o*-phenylenediamine with benzaldehyde instead of alcohol in the absence of catalyst gave 85% of 2-phenylbenzimidazole (entry 14, Table 6). This confirmed that ruthenium catalyst is mainly involved in the oxidation of alcohols to aldehydes. Further experiments are ongoing to explain these results.

## Conclusions

We have reported the synthesis and characterization of novel air-stable complexes  $[\text{RuCl}(\text{CO})(\text{EPh}_3)(\text{L})]$  (**1–6**), in which the substituent's on the terminal position of the ligands

and coligands have been modified. The crystal structures of three of the complexes prepared, **1**, **2**, **6** have been described. The catalytic study of  $[\text{RuCl}(\text{CO})(\text{EPh}_3)(\text{L})]$  complexes **1–6** toward amine *N*-alkylation and one-pot synthesis of benzoxazoles was completed, showing that all catalysts are active toward catalytic transformations. The results also showed that steric effects in the ligands play a more important role than electronic effects in the catalytic activity of the new complexes. In the *N*-alkylation process, the complex **2** has been proven to be versatile and efficient catalysts under mild conditions in comparison to its analogues and other ruthenium and iridium complexes<sup>50</sup>. Also, the complex **2** has shown high tolerance to functional groups in the amine and alcohol moieties. The present process is applicable for the direct amination of 2-nitropyridine with benzyl alcohol leading to the secondary amine with **2** as the catalyst. Furthermore, the complex **2** has been proven to selectively catalyze the synthesis of *N,N*-dialkylated amine when diamine are used as substrates. On the other hand, complex **2** have been proven to be very efficient and versatile catalyst for the synthesis of 2-substituted benzimidazoles, benzoxazoles and benzothiazoles.

## Experimental Section

### General

Unless otherwise noted, all reactions were performed under an atmosphere of air. Thin-layer chromatography (TLC) was performed 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 analyses (C, H, N, S) were performed 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  $\text{cm}^{-1}$  using a Nicolet Avatar model FT-IR spectrophotometer. The electronic spectra of the complexes were recorded with a Shimadzu UV–1650 PC spectrophotometer using dichloromethane as the solvent.  $^1\text{H}$  (300 and 400 MHz),  $^{13}\text{C}$  (100 MHz) and  $^{31}\text{P}$  NMR (162 MHz) spectra were taken in DMSO or  $\text{CDCl}_3$  at room temperature with a Bruker AV400 instrument with chemical shifts relative to tetramethylsilane ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and *o*-phosphoric acid ( $^{31}\text{P}$ ). Mass spectra were recorded on a LC–MS Q–ToF Micro Analyzer (Shimadzu), using electrospray ionization (ESI) mode. GC–Mass was performed using a JEOL GCMATE II GC–MS system. The melting points were recorded with a Lab India melting point apparatus.

Commercially available  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  was used as supplied from Loba Chemie Pvt. Ltd. All the reagents used in this study were Analar grade, and the solvents were purified and dried according to standard procedures. Triphenylphosphine/triphenylarsine, 2-(diphenylphosphino)-benzaldehyde and thiosemicarbazone derivatives were purchased from Aldrich and were used as received. The ruthenium metallic precursors  $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$  and  $[\text{RuHCl}(\text{CO})(\text{AsPh}_3)_3]$  were prepared according to literature methods.<sup>51</sup>

### Synthesis of the ligands

The ligands 2-(2-(diphenylphosphino)benzylidene) thiosemicarbazone (**PNS-H**) and 2-(2-(diphenylphosphino)benzylidene)-*N*-methylthiosemicarbazone (**PNS-Me**) 2-(2-(diphenylphosphino)benzylidene)-*N*-phenylthiosemicarbazone (**PNS-Ph**) were prepared following the procedure reported before.<sup>9-15</sup>

### Synthesis of the complexes

**$[\text{RuCl}(\text{CO})(\text{PPh}_3)(\text{PNS-H})]$  (1).** A suspension of  $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$  (0.100 g, 0.105 mmol) in ethanol (15 mL) was treated with **PNS-H** (0.038 g, 0.105 mmol) and the mixture was gently refluxed for 6h. During this time the color changed to orange. After it was cooled to room temperature, the suspension was filtered and the orange solid was thoroughly washed with cold ethanol and diethyl ether. Yield 78% (0.10 g), mp: 256–258 °C. Anal. Calcd for  $\text{C}_{39}\text{H}_{32}\text{ClN}_3\text{OP}_2\text{RuS}$ : C, 59.35; H, 4.09; N, 5.32; S, 4.06. Found: C, 59.49; H, 4.12; N, 5.14; S, 4.26. IR (KBr disks,  $\text{cm}^{-1}$ ): 3434 (ms,  $\nu_{\text{NH}}$ ); 3064 (m,  $\nu_{\text{NH}}$ ); 1949 (s,  $\nu_{\text{C}\equiv\text{O}}$ ); 1582 + 1474 (s,  $\nu_{\text{C}=\text{N}}$  +  $\nu_{\text{C}-\text{N}}$ ); 742 (s,  $\nu_{\text{C}-\text{S}}$ ); 1434, 1089, 693 (s, for  $\text{PPh}_3$ ). UV-Vis ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  (nm): 234, 258, 343, 427.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) = 8.73 (d, 1H,  $J$  = 8.8 Hz, CH=N), 8.50 (s,  $-\text{NH}_2$ ), 7.71–7.53 (m, 4H, Ar H), 7.49–7.19 (m, 14H, Ar H), 7.13–7.09 (m, 4H, Ar H), 6.67 (t, 7H,  $J$  = 8.0 Hz, Ar H), 6.55–6.51 (m, 4H, Ar H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) = 206.73 (C $\equiv$ O), 176.12 (C–S), 154.60 ( $-\text{CH}=\text{N}$ ), 138.82 (Ar C), 137.43 (Ar C), 137.24 (Ar C), 136.05 (Ar C), 135.70 (Ar C), 135.60 (Ar C), 133.50 (Ar C), 133.36 (Ar C), 132.94 (Ar C), 129.87 (Ar C), 129.12 (Ar C), 129.01 (Ar C), 128.85 (Ar C), 128.78 (Ar C), 128.01 (Ar C), 127.44 (Ar C), 125.55 (Ar C), 125.26 (Ar C).  $^{31}\text{P}$  NMR (162 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) = 30.05 (d,  $J$  = 22.6 Hz,  $\text{PPh}_3$ ), 28.74 (d,  $J$  = 22.6 Hz,  $\text{PPh}_2$ ). MS (ESI,  $m/z$ ): 753.6  $[\text{M} - \text{Cl}]^+$ . Single

crystals suitable for an X-ray determination were grown by slow evaporation of dichloromethane-methanol solution of **1** at room temperature.

**[RuCl(CO)(PPh<sub>3</sub>)(PNS-Me)] (2)**. It was prepared as described for **1** by the suspension of [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] (0.100 g, 0.105 mmol) with **PNS-Me** (0.039 g, 0.105 mmol). Yield 73% (0.10 g), mp: 254–256 °C. Anal. Calcd for C<sub>40</sub>H<sub>34</sub>ClN<sub>3</sub>OP<sub>2</sub>RuS: C, 59.81; H, 4.27; N, 5.23; S, 3.99. Found: C, 59.49; H, 4.09; N, 5.14; S, 4.26. IR (KBr disks, cm<sup>-1</sup>): 3420 (ms, ν<sub>NH</sub>); 1945 (s, ν<sub>C≡O</sub>); 1584 + 1471 (s, ν<sub>C=N</sub> + ν<sub>C-N</sub>); 747 (s, ν<sub>C-S</sub>); 1432, 1091, 695 (s, PPh<sub>3</sub>). UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>), λ<sub>max</sub> (nm): 233, 245, 355, 430. <sup>1</sup>H NMR (400MHz, DMSO): δ (ppm) = 8.75 (d, 1H, *J* = 8.0 Hz, -CH=N); 8.57 (s, 1H, -NH), 7.62–7.58 (m, 1H, Ar H), 7.56–7.13 (m, 24H, Ar H), 6.89 (t, 2H, *J* = 10.8 Hz, Ar H), 6.78 (t, 1H, *J* = 11.2 Hz, Ar H), 6.72 (t, 2H, *J* = 11.6 Hz, Ar H), 1.22 (s, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ (ppm) = 206.48 (C≡O), 176.45 (C-S), 155.53 (-CH=N), 136.48 (Ar C), 135.27 (Ar C), 133.84 (Ar C), 132.17 (Ar C), 131.95 (Ar C), 130.71 (Ar C), 130.61 (Ar C), 130.55 (Ar C), 130.38 (Ar C), 130.27, Ar C), 129.65 (Ar C), 127.91 (Ar C), 127.86 (Ar C), 127.79 (Ar C), 127.65 (Ar C), 127.53 (Ar C), 127.30 (Ar C), 126.51 (Ar C), 126.33 (Ar C), 125.45 (Ar C), 123.81 (Ar C), 123.53 (Ar C), 31.17 (-CH<sub>3</sub>). <sup>31</sup>P NMR (162 MHz, DMSO-d<sub>6</sub>): δ (ppm) = 30.15 (d, *J* = 22.6 Hz, PPh<sub>3</sub>), 28.85 (d, *J* = 25.9 Hz, PPh<sub>2</sub>). MS (ESI, *m/z*): 794.1 [M - Cl]<sup>+</sup>. Orange colored crystals obtained in the reaction mixture itself were found to be suitable for X-ray diffraction.

**[RuCl(CO)(PPh<sub>3</sub>)(PNS-Ph)] (3)**. It was prepared as described for **1** by the suspension of [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] (0.100 g, 0.105 mmol) with **PNS-Ph** (0.039 g, 0.105 mmol). Yield 78% (0.10 g), mp: 254–256 °C. Anal. Calcd for C<sub>45</sub>H<sub>36</sub>ClN<sub>3</sub>OP<sub>2</sub>RuS: C, 62.46; H, 4.19; N, 4.86; S, 3.71. Found: C, 62.61; H, 4.21; N, 4.94; S, 3.91. IR (KBr disks, cm<sup>-1</sup>): 3390 (ms, ν<sub>NH</sub>); 1962 (s, ν<sub>C≡O</sub>); 1591 + 1482 (s, ν<sub>C=N</sub> + ν<sub>C-N</sub>); 738 (s, ν<sub>C-S</sub>); 1433, 1092, 694 (s, PPh<sub>3</sub>). UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>), λ<sub>max</sub> (nm): 236, 256, 369, 428. <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>): δ (ppm) = 8.75 (d, 1H, *J* = 8.7 Hz, -CH=N), 8.60 (s, 1H, -NH), 7.68 (d, 2H, *J* = 8.4 Hz, Ar H), 7.63 (s, 2H, Ar H), 7.57–7.46 (m, 9H, Ar H), 7.33 (t, 6H, *J* = 6.3 Hz, Ar H), 7.25–7.16 (m, 9H, Ar H), 7.06 (t, 2H, *J* = 7.2 Hz, Ar H), 6.90 (t, 1H, *J* = 6.9 Hz, Ar H), 6.78 (t, 1H, *J* = 8.4 Hz, Ar H), 6.59 (t, 2H, *J* = 8.7 Hz, Ar H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ (ppm) = 206.40 (C≡O), 170.42 (C-S), 156.56 (-CH=N), 136.93 (Ar C), 136.76 (Ar C), 136.13 (Ar C), 136.05 (Ar C), 134.39 (Ar C), 133.81 (Ar C), 133.73 (Ar C), 133.50 (Ar C), 133.40 (Ar C), 133.30 (Ar C), 133.27 (Ar C), 133.08 (Ar C),



132.00 (Ar C), 131.90 (Ar C), 131.68 (Ar C), 131.30 (Ar C), 131.15 (Ar C), 130.58 (Ar C), 130.24 (Ar C), 129.96 (Ar C), 128.90 (Ar C), 128.91 (Ar C), 128.73 (Ar C), 128.66 (Ar C), 128.57 (Ar C), 128.48 (Ar C), 128.30 (Ar C), 128.05 (Ar C), 127.95 (Ar C), 127.75 (Ar C), 127.66 (Ar C), 126.66 (Ar C), 126.24 (Ar C), 121.16 (Ar C), 119.07 (Ar C).  $^{31}\text{P}$  NMR (162 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) = 29.79 (d,  $J$  = 22.6 Hz, PPh $_3$ ), 28.85 (d,  $J$  = 22.6 Hz, PPh $_2$ ). MS (ESI,  $m/z$ ): 830.2 [M – Cl] $^+$ .

**[RuCl(CO)(AsPh $_3$ )(PNS-H)] (4).** A suspension of [RuHCl(CO)(AsPh $_3$ ) $_3$ ] (0.100 g, 0.105 mmol) in ethanol (15 mL) was treated with **PNS-H** (0.038 g, 0.105 mmol) and the mixture was gently refluxed for 8 h. During this time the colour changed to yellow. Then the solvent was removed under reduced pressure, and the solid was washed thoroughly with cold ethanol and diethyl ether, affording a shiny yellow crystalline solid. Yield 82% (0.11 g), mp: 110–112 °C. Anal. Calcd for C $_{39}$ H $_{32}$ AsClN $_3$ OPRuS: C, 56.22; H, 3.87; N, 5.04; S, 3.85. Found: C, 56.49; H, 3.79; N, 5.14; S, 3.66. IR (KBr disks,  $\text{cm}^{-1}$ ): 3392 (ms,  $\nu_{\text{NH}}$ ); 1962 (s,  $\nu_{\text{C}\equiv\text{O}}$ ); 1592 + 1496 (s,  $\nu_{\text{C}=\text{N}}$  +  $\nu_{\text{C}-\text{N}}$ ); 738 (s,  $\nu_{\text{C}-\text{S}}$ ); 1433, 1092, 694 (s, for AsPh $_3$ ). UV–Vis (CH $_2$ Cl $_2$ ),  $\lambda_{\text{max}}$  (nm): 231, 245, 350, 427.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) = 8.86 (d, 1H,  $J$  = 8.3 Hz, –CH=N), 8.48 (s, 1H, –NH $_2$ ), 7.86 (t, 1H,  $J$  = 7.2 Hz, Ar H), 7.75–7.02 (m, 23H, Ar H), 6.89 (t, 3H,  $J$  = 7.2 Hz, Ar H), 6.70 (t, 1H,  $J$  = 8.8 Hz, Ar H), 6.57 (m, 2H,  $J$  = 7.2 Hz, Ar H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) = 206.02 (C $\equiv$ O), 176.04 (C–S), 154.59 (–CH=N), 138.91 (Ar C), 136.53 (Ar C), 134.41 (Ar C), 134.02 (Ar C), 133.92 (Ar C), 133.52 (Ar C), 133.19 (Ar C), 133.11 (Ar C), 132.08 (Ar C), 131.81 (Ar C), 131.16 (Ar C), 130.64 (Ar C), 130.39 (Ar C), 130.02 (Ar C), 128.84 (Ar C), 128.66 (Ar C), 128.51 (Ar C), 128.17 (Ar C), 128.08 (Ar C), 125.21 (Ar C).  $^{31}\text{P}$  NMR (162 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) = 32.13 (s, PPh $_2$ ). MS (ESI,  $m/z$ ): 767.6 [M – Cl] $^+$ .

**[RuCl(CO)(AsPh $_3$ )(PNS-Me)] (5).** It was prepared as described for **4** by the suspension of [RuHCl(CO)(AsPh $_3$ ) $_3$ ] (0.100 g, 0.092 mmol) with **PNS-Me** (0.034 g, 0.092 mmol). Yield 78% (0.10 g), mp: 120–122 °C. Anal. Calcd for C $_{40}$ H $_{34}$ AsClN $_3$ OPRuS: C, 56.71; H, 4.05; N, 4.96; S, 3.78. Found: C, 56.87; H, 4.31; N, 4.81; S, 3.26. IR (KBr disks,  $\text{cm}^{-1}$ ): 3423 (ms,  $\nu_{\text{NH}}$ ); 1945 (s,  $\nu_{\text{C}\equiv\text{O}}$ ); 1585 + 1490 (s,  $\nu_{\text{C}=\text{N}}$  +  $\nu_{\text{C}-\text{N}}$ ); 747 (s,  $\nu_{\text{C}-\text{S}}$ ); 1432, 1091, 695 (s, for AsPh $_3$ ). UV–Vis (CH $_2$ Cl $_2$ ),  $\lambda_{\text{max}}$  (nm): 235, 257, 356, 435.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) = 8.77 (d, 1H,  $J$  = 8.0 Hz, –CH=N), 8.15 (s, 1H, –NH), 7.63–7.10 (m, 24H, Ar H), 6.89–6.86 (m, 1H, Ar H),

6.72 (t, 1H,  $J = 7.6$  Hz, Ar H), 6.55 (t, 2H,  $J = 8.0$  Hz, Ar H), 1.22 (s, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) = 206.42 ( $\text{C}\equiv\text{O}$ ), 176.03 ( $\text{C-S}$ ), 154.27 ( $-\text{CH}=\text{N}$ ), 138.91 (Ar C), 134.00 (Ar C), 133.90 (Ar C), 133.79 (Ar C), 133.54 (Ar C), 133.12 (Ar C), 132.91 (Ar C), 132.80 (Ar C), 131.79 (Ar C), 131.68 (Ar C), 131.38 (Ar C), 131.29 (Ar C), 131.03 (Ar C), 130.48 (Ar C), 130.32 (Ar C), 129.89 (Ar C), 129.06 (Ar C), 128.64 (Ar C), 128.41 (Ar C), 128.10 (Ar C), 128.00 (Ar C), 30.60 ( $-\text{CH}_3$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) = 32.73 (s,  $\text{PPh}_2$ ). MS (ESI,  $m/z$ ): 811.8  $[\text{M} - \text{Cl}]^+$ .

**[RuCl(CO)(AsPh<sub>3</sub>)(PNS-Ph)] (6).** It was prepared as described for **4** by the suspension of  $[\text{RuHCl}(\text{CO})(\text{AsPh}_3)_3]$  (0.100 g, 0.092 mmol) with **PNS-Ph** (0.039 g, 0.092 mmol). Yield 76% (0.105 g), mp: 132–134 °C. Anal. Calcd for  $\text{C}_{45}\text{H}_{36}\text{AsClN}_3\text{OPRuS}$ : C, 59.44; H, 3.99; N, 4.62; S, 3.53. Found: C, 59.28; H, 3.89; N, 4.81; S, 3.26. IR (KBr disks,  $\text{cm}^{-1}$ ): 3390 (ms,  $\nu_{\text{NH}}$ ); 1962 (s,  $\nu_{\text{C}\equiv\text{O}}$ ); 1591 + 1482 (s,  $\nu_{\text{C}=\text{N}} + \nu_{\text{C}-\text{N}}$ ); 738 (s,  $\nu_{\text{C}-\text{S}}$ ); 1433, 1092, 694 (s, for  $\text{AsPh}_3$ ). UV–Vis ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  (nm): 235, 258, 367, 429.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) = 8.74 (d, 1H,  $J = 7.6$  Hz,  $-\text{CH}=\text{N}$ ), 8.52 (s, 1H,  $-\text{NH}$ ), 7.88–7.85 (m, 1H, Ar H), 7.74 (d, 2H,  $J = 7.6$  Hz, Ar H), 7.63–7.10 (m, 27H, Ar H), 6.89 (t, 1H,  $J = 7.2$  Hz, Ar H), 6.72–6.60 (m, 1H, Ar H), 6.57 (t, 2H,  $J = 8.8$  Hz, Ar H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) = 206.45 ( $\text{C}\equiv\text{O}$ ), 170.73 ( $\text{C-S}$ ), 155.68 ( $-\text{CH}=\text{N}$ ), 135.48 (Ar C), 135.27 (Ar C), 133.84 (Ar C), 132.35 (Ar C), 131.17 (Ar C), 129.95 (Ar C), 124.40 (Ar C), 123.71 (Ar C), 123.61 (Ar C), 123.55 (Ar C), 123.38 (Ar C), 123.27 (Ar C), 122.65 (Ar C), 122.51 (Ar C), 122.36 (Ar C), 122.11 (Ar C), 121.89 (Ar C), 121.53 (Ar C), 121.20 (Ar C), 121.11 (Ar C), 120.73 (Ar C), 120.45 (Ar C), 119.02 (Ar C), 116.81 (Ar C), 115.82 (Ar C).  $^{31}\text{P}$  NMR (162 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) = 31.38 (s,  $\text{PPh}_2$ ). MS (ESI,  $m/z$ ): 873.0  $[\text{M} - \text{Cl}]^+$ . Single crystals suitable for an X-ray determination were grown by slow evaporation of dichloromethane-ethanol solution of **6** at room temperature.

## Catalysis

### Catalytic *N*-alkylation of (hetero)aromatic amines and amide with alcohols

A typical procedure is as follows. To a stirred suspension of ruthenium(II) catalyst (0.5 mol %) and KOH (4 mmol) in toluene (5 mL) were added alcohol (2.0 mmol), amine/amide (2.0 mmol) at room temperature and then temperature was raised to 100 °C for 12 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature,  $\text{H}_2\text{O}$  (3 mL) was

added and the organic layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The combined organic layers were dried with magnesium sulphate and concentrated. The crude product was analyzed by GC-MS or purified by Column chromatography (n-hexane/EtOAc). Reported isolated yields are an average of two runs.

#### **Direct amination of 2-nitropyridine with benzyl alcohol**

To a stirred suspension of ruthenium(II) catalyst (0.5 mol %) and KOH (4 mmol) in toluene (5 mL) were added benzyl alcohol (12.0 mmol), 2-nitropyridine (2.0 mmol) at room temperature and then temperature was raised to 100 °C for 12 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature,  $\text{H}_2\text{O}$  (3 mL) was added and the organic layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The combined organic layers were dried with magnesium sulphate and concentrated. The crude product was analyzed by GC-MS or purified by Column chromatography (n-hexane/EtOAc). Reported isolated yields are an average of two runs.

#### **Catalytic *N*-alkylation of hetero aromatic diamine with alcohols**

To a stirred suspension of ruthenium(II) catalyst (0.1 mol %) and KOH (4 mmol) in toluene (5 mL) were added alcohol (4 mmol), diamine (2.0 mmol) at room temperature and then temperature was raised to 120 °C for 12 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature,  $\text{H}_2\text{O}$  (3 mL) was added and the organic layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The combined organic layers were concentrated *in vacuo* and the crude product was analyzed by GC-MS or purified by Column chromatography over silica-gel (n-hexane/ethyl acetate). Reported isolated yields are an average of two runs.

#### **Typical procedure for the one-pot synthesis of 2-substituted benzazoles**

To a stirred suspension of ruthenium catalyst (0.5 mol %) and KOH (4 mmol) in toluene (5 mL) were added alcohol (3 mmol), *o*-substituted aniline (2.0 mmol) at room temperature and then temperature was raised to 120 °C for 24 h. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature,  $\text{H}_2\text{O}$  (3 mL) was added and the organic layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The combined organic layers were concentrated *in vacuo*

and the crude product was analyzed by GC-MS or purified by Column chromatography (n-hexane/EtOAc). Reported isolated yields are an average of two runs.

The catalytic reactions given in Tables 3–7 were similarly conducted. The resulting amines, amides, 2- aryl substituted benzimidazoles, benzoxazoles and benzothiazoles were identified by comparison of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data with those previously reported (S33–S60, ESI†).

### X-ray Crystallography

Crystals of **1**, **2** and **6** were mounted on glass fibers and used for data collection. Crystal data were collected at 295.0(2) K (**1**, **6**) using a Gemini A Ultra Oxford Diffraction automatic diffractometer or at 293.0(2) (2) K using a Stoe Mark II-Image Plate Diffraction system. Graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) 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-97.<sup>52</sup> Refinement and all further calculations were carried out using SHELXL-97.<sup>52</sup> 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  $F^2$ . Atomic scattering factors were incorporated in the computer programs. In the solid state (**1** and **2**), a disorder is observed within the two different enantiomeric forms in such a manner that only the CO group and the chlorine atom share the ligand positions mutually. Despite several attempts to get better crystals of complex **6** and a better data set, only poor-quality data were obtained.

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### Electronic supplementary information (ESI) available:

$^1\text{H}$  and  $^{13}\text{C}$ -NMR spectrum of ligands (**PNS-H**, **PNS-Me**, **PNS-Ph**) and complexes (**1-6**),  $^{31}\text{P}$ -NMR and ESI-MS spectrum of complexes (**1-6**), general experimental procedures and

characterization data for *N*-alkylated products. CCDC reference numbers 969003, 969004 and 969005. For ESI and crystallographic data in CIF or other electronic format see DOI

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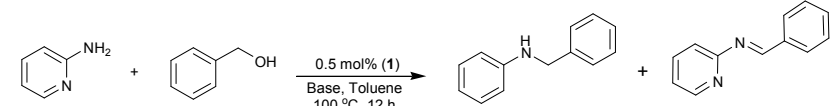
**Table 1** Crystal data and structure refinement parameters for complexes **1**, **2** and **6**

	<b>1</b>	<b>2</b>	<b>6</b>
CCDC number	969003	969004	969005
Empirical formula	C <sub>39</sub> H <sub>32</sub> ClN <sub>3</sub> OP <sub>2</sub> RuS. 0.5(C <sub>2</sub> H <sub>8</sub> O <sub>2</sub> )	C <sub>40</sub> H <sub>34</sub> ClN <sub>3</sub> OP <sub>2</sub> RuS	C <sub>45</sub> H <sub>36</sub> AsClN <sub>3</sub> OPRuS
Formula weight	821.24	803.22	909.24
<i>T</i> (K)	295	298	295
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
Unit cell dimensions			
<i>a</i> (Å)	14.3822(5)	14.3388(8)	10.2991(8)
<i>b</i> (Å)	16.6752(6)	16.6137(6)	13.1254(11)
<i>c</i> (Å)	15.1543(4)	15.0818(8)	15.2952(13)
$\alpha$ (°)	90.00	90.00	97.686(7)
$\beta$ (°)	96.312(3)	96.268(4)	94.380(7)
$\gamma$ (°)	90.00	90.00	96.521(7)
Volume (Å <sup>3</sup> )	3612.4(2)	3571.3(3)	2027.0(3)
<i>Z</i>	4	4	2
Density (calculated) Mg m <sup>-3</sup>	1.510	1.494	1.490
Absorption coefficient mm <sup>-1</sup>	0.695	0.699	1.392
<i>F</i> (000)	1680	1640	920
scan range for data collection (deg)	3.42 to 25.05	1.83 to 24.99	3.62 to 28.70
Index ranges	-17 < = <i>h</i> < = 17 -19 < = <i>k</i> < = 18 -17 < = <i>l</i> < = 18	-17 < = <i>h</i> < = 17 -19 < = <i>k</i> < = 18 -17 < = <i>l</i> < = 17	-12 < = <i>h</i> < = 12 -15 < = <i>k</i> < = 15 -16 < = <i>l</i> < = 18
Reflections collected/unique, <i>R</i> <sub>int</sub>	18987/6367,0.0353	40742/6289,0.1379	14624/7165,0.0673
Completeness to theta <sub>max</sub>	0.997	0.994	0.996
Data/restraints/parameters	6367/0/486	6289/0/382	7165/0/487
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.060	0.994	1.070
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.035, w <i>R</i> <sub>2</sub> = 0.081	<i>R</i> <sub>1</sub> = 0.056, w <i>R</i> <sub>2</sub> = 0.101	<i>R</i> <sub>1</sub> = 0.056, w <i>R</i> <sub>2</sub> = 0.114
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.047, w <i>R</i> <sub>2</sub> = 0.086	<i>R</i> <sub>1</sub> = 0.093, w <i>R</i> <sub>2</sub> = 0.111	<i>R</i> <sub>1</sub> = 0.076, w <i>R</i> <sub>2</sub> = 0.122
<sup>a</sup> Structures were refined on <i>F</i> <sub>o</sub> <sup>2</sup> : w <i>R</i> <sub>2</sub> = [∑[w( <i>F</i> <sub>o</sub> <sup>2</sup> - <i>F</i> <sub>c</sub> <sup>2</sup> ) <sup>2</sup> ] / ∑w( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sup>2</sup> ] <sup>1/2</sup> , where w <sup>-1</sup> = [∑( <i>F</i> <sub>o</sub> <sup>2</sup> ) + ( <i>aP</i> ) <sup>2</sup> + <i>bP</i> ] and <i>P</i> = [max( <i>F</i> <sub>o</sub> <sup>2</sup> , 0) + 2 <i>F</i> <sub>c</sub> <sup>2</sup> ]/3.			

**Table 2** Selected geometrical parameters for complexes **1**, **2** and **6**

<b>1</b>		<b>2</b>		<b>6</b>	
Interatomic distances (Å)					
Ru(1)–C(1A) <sup>a</sup>	1.88(2)	Ru(1)–C(41) <sup>a</sup>	1.8183	Ru(1)–C(1)	1.89(3)
Ru(1)–C(1B) <sup>a</sup>	1.809(18)	Ru(1)–C(41A) <sup>a</sup>	1.8384	-	-
Ru(1)–N(1)	2.125(3)	Ru(1)–N(1)	2.128(4)	Ru(1)– N(1)	2.02(2)
Ru(1)–P(1)	2.344(8)	Ru(1)–P(1)	2.3429	Ru(1)– P(1)	2.333(8)
Ru(1)–S(1)	2.386(8)	Ru(1)–S(1)	2.3882	Ru(1)– S(1)	2.393(8)
Ru(1)–P(2)	2.398(8)	Ru(1)–P(2)	2.3929	Ru(1)– As(1)	2.469(4)
Ru(1)–Cl(1) <sup>a</sup>	2.441(4)	Ru(1)–Cl(1) <sup>a</sup>	2.4181	Ru(1)– Cl(1)	2.425(9)
Ru(1)–Cl(2) <sup>a</sup>	2.397(5)	Ru(1)–Cl(1A) <sup>a</sup>	2.4478	-	-
Bond angles(°)					
C(1B)–Ru(1)–N(1)	87.4(6)	C(41)–Ru(1)–P(1)	91.3	C(1)–Ru(1)– N(1)	89.6(10)
C(1B)–Ru(1)–P(1)	91.1(6)	C(41)– Ru(1) –S(1)	89.3	C(1)– Ru(1)– P(1)	92.4(8)
C(1B)–Ru(1)–S(1)	90.2(6)	C(41)– Ru(1)– P(2)	90.3	C(1)–Ru(1)– S(1)	91.3(8)
C(1B)–Ru(1)–P(2)	90.2(6)	C(41)– Ru(1)– Cl(1A) <sup>a</sup>	168.9	C(1)– Ru(1)– Cl(1)	174.5(8)
C(1B)–Ru(1)–Cl(1) <sup>a</sup>	166.6(6)	N(1) –Ru(1)– C(41)	87.01(11)	C(1)– Ru(1)– As(1)	88.5(8)
C(1B)–Ru(1)–Cl(2) <sup>a</sup>	173.7(5)	C(41A)– Ru(1)– Cl(1) <sup>a</sup>	169.6	-	-
N(1)–Ru(1)–P(1)	90.63(7)	N(1)– Ru(1)– P(1)	91.04(11)	N(1)– Ru(1)– P(1)	92.0(6)
N(1)–Ru(1)–S(1)	81.21(7)	N(1)– Ru(1)– S(1)	81.15(11)	N(1)– Ru(1)– S(1)	79.0(6)
N(1)–Ru(1)–P(2)	169.37(7)	N(1)– Ru(1)– P(2)	168.74(11)	N(1)– Ru(1)– Cl(1)	85.0(7)
N(1)–Ru(1)–Cl(1)	79.29(16)	N(1)– Ru(1)– Cl(1)	85.08(11)	N(1)–Ru(1)– As(1)	166.3(6)
P(1)–Ru(1)–S(1)	171.67(3)	P(1)– Ru(1)– S(1)	172.1	P(1)–Ru(1)– S(1)	170.2(3)
P(1)–Ru(1)–P(2)	99.78(3)	P(1)– Ru(1)– P(2)	100.0	P(1)–Ru(1)– Cl(1)	86.9(3)
P(1)–Ru(1)–Cl(1)	87.63(8)	P(1)– Ru(1)– Cl(1)	91.8	P(1)–Ru(1)– As(1)	101.7(2)
S(1)–Ru(1)–P(2)	88.45(3)	S(1)– Ru(1)– P(2)	87.9	S(1)–Ru(1)– Cl(1)	88.6(3)
S(1)–Ru(1)–Cl(1)	89.22(8)	S(1)– Ru(1)– Cl(1)	88.6	S(1)–Ru(1)– As(1)	87.5(2)
P(2)–Ru(1)–Cl(1)	103.15(14)	P(2)– Ru(1)– Cl(1)	92.1	Cl(1)–Ru(1)– As(1)	97.0(2)

<sup>a</sup>The molecular structures **1** and **2** shows a disorder in which the Cl ligand and CO ligand have two orientations in about 51:49 and 55:45 ratio for **1** and **2**, respectively.

**Table 3** Optimization of N-alkylation reaction Conditions<sup>a</sup>


Entry	Base	Alcohol/amine /base	Yield (%) <sup>b</sup>	Amine (%) <sup>c</sup>
1	-	1:1	0	-
2	K <sub>2</sub> CO <sub>3</sub>	1:1:1	0	-
3	K <sub>2</sub> CO <sub>3</sub>	1:1:2	0	-
4	K <sub>2</sub> CO <sub>3</sub>	1:1:3	0	-
5	KOH	1:1:1	90	86
6	KOH	1:1:1.5	92	90
7	<b>KOH</b>	<b>1:1:2</b>	<b>94</b>	<b>94</b>
8	KOH	1:1:3	94	94
9	KO <i>t</i> -Bu	1:1:1	88	62
10	KO <i>t</i> -Bu	1:1:1.5	93	67
11	KO <i>t</i> -Bu	1:1:2	96	74
12	KO <i>t</i> -Bu	1:1:3	95	75
13	NaOH	1:1:2	95	78
14	NaHCO <sub>3</sub>	1:1:2	0	-

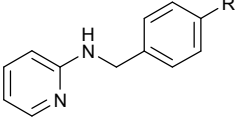
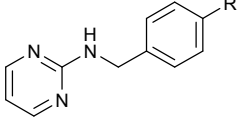
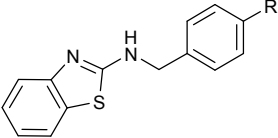
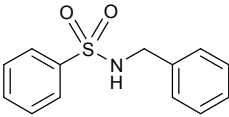
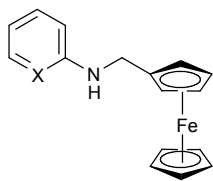
<sup>a</sup> Reaction conditions: 2.00 mmol of benzyl alcohol, 2.00 mmol of 2-aminopyridine, Base (4 mmol), catalyst **1** (0.5 mol %) in 5 mL of toluene at 100 °C. <sup>b</sup> Based on GC-MS of crude reaction mixture. <sup>c</sup> Conversions determined by GC-MS. Formation of the corresponding imine as a byproduct accounts for the difference in conversion.

**Table 4** Influence of terminal substituent's, coligands and catalyst loading on the catalytic activity of ruthenium(II) Complexes<sup>a</sup>

Entry	[Ru]	Terminal substituent's (R)/coligands	Amount [Ru] (mol%)	Time (h)	Yield (%) <sup>b</sup>	Amine (%) <sup>c</sup>
1	-	-	-	24	-	-
2	<b>1</b>	H/PPh <sub>3</sub>	0.1	24	71	52
3	<b>2</b>	Me/PPh <sub>3</sub>	0.1	24	64	61
4	<b>3</b>	Ph/PPh <sub>3</sub>	0.1	24	59	59
5	<b>4</b>	H/AsPh <sub>3</sub>	0.1	24	68	45
6	<b>5</b>	Me/AsPh <sub>3</sub>	0.1	24	67	59
7	<b>6</b>	Ph/AsPh <sub>3</sub>	0.1	24	56	54
8	<b>1</b>	H/PPh <sub>3</sub>	0.3	18	89	62
9	<b>2</b>	Me/PPh <sub>3</sub>	0.3	18	84	82
10	<b>3</b>	Ph/PPh <sub>3</sub>	0.3	18	75	76
11	<b>4</b>	H/AsPh <sub>3</sub>	0.3	18	87	59
12	<b>5</b>	Me/AsPh <sub>3</sub>	0.3	18	83	78
13	<b>6</b>	Ph/AsPh <sub>3</sub>	0.3	18	74	74
14	<b>1</b>	H/PPh <sub>3</sub>	0.5	12	83	82
<b>15</b>	<b>2</b>	<b>Me/PPh<sub>3</sub></b>	<b>0.5</b>	<b>12</b>	<b>&gt;99</b>	<b>&gt;99</b>
16	<b>3</b>	Ph/PPh <sub>3</sub>	0.5	12	92	91
17	<b>4</b>	H/AsPh <sub>3</sub>	0.5	12	81	78
18	<b>5</b>	Me/AsPh <sub>3</sub>	0.5	12	97	97
19	<b>6</b>	Ph/AsPh <sub>3</sub>	0.5	12	90	89

<sup>a</sup> N-alkylation reaction conditions: 2.00 mmol of benzyl alcohol, 2.00 mmol of 2-amino pyridine, KOH (4 mmol), catalyst (0.1-0.5 mol %) in 5 mL of toluene at 100 °C. <sup>b</sup>Based on GC-MS of crude reaction mixture. <sup>c</sup>Conversions determined by GC-MS. Formation of the corresponding imine as a byproduct accounts for the difference in conversion.

**Table 5** *N*-alkylation of (hetero) aromatic amine/amide with alcohols catalyzed by **2**<sup>a,b</sup>

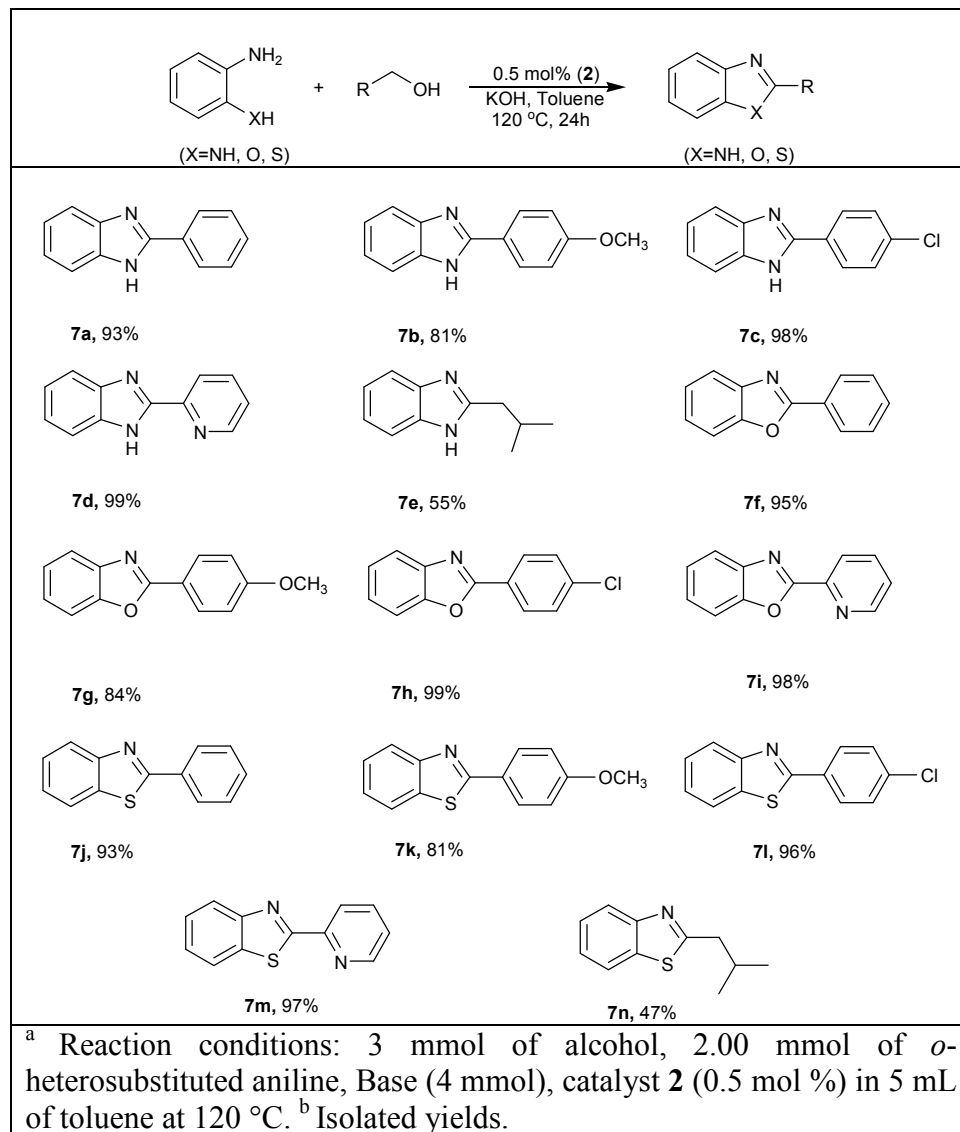
$\text{R-NH}_2 + \text{R}'\text{-OH} \xrightarrow[\text{100 } ^\circ\text{C, 12 h}]{\text{0.5 mol\% (2), KOH, Toluene}} \text{R}'\text{-N(R)-H}$	
 <p> <b>1a</b> (R=H), 92%  <b>1b</b> (R=CH<sub>3</sub>), 78%  <b>1c</b> (R=OCH<sub>3</sub>), 81%  <b>1d</b> (R=Cl), 96%  <b>1e</b> (R=Br), 93%         </p>	 <p> <b>2a</b> (R=H), 97%  <b>2b</b> (R=CH<sub>3</sub>), 86%  <b>2c</b> (R=OCH<sub>3</sub>), 83%  <b>2d</b> (R=Cl), 98%  <b>2e</b> (R=Br), 95%         </p>
 <p> <b>3a</b> (R=H), 92%  <b>3b</b> (R=CH<sub>3</sub>), 81%  <b>3c</b> (R=OCH<sub>3</sub>), 79%  <b>3d</b> (R=Cl), 97%  <b>3e</b> (R=Br), 94%         </p>	 <p> <b>4a</b> (R=H), 90%  <b>4b</b> (R=CH<sub>3</sub>), 88%  <b>4c</b> (R=OCH<sub>3</sub>), 76%  <b>4d</b> (R=Cl), 99%  <b>4e</b> (R=Br), 95%         </p>
 <p> <b>5a</b> (X=N, R=H), 82%  <b>5b</b> (X=H, R=H), 77%  <b>5c</b> (X=H, R=CH<sub>3</sub>), 68%  <b>5d</b> (X=H, R=Cl), 91%  <b>5e</b> (X=H, R=Br), 86%         </p>	
<p><sup>a</sup> Reaction conditions: 2.00 mmol of alcohol, 2.00 mmol of amine/amide, Base (4 mmol), catalyst <b>2</b> (0.5 mol %) in 5 mL of toluene at 100 °C. <sup>b</sup> Isolated yields.</p>	

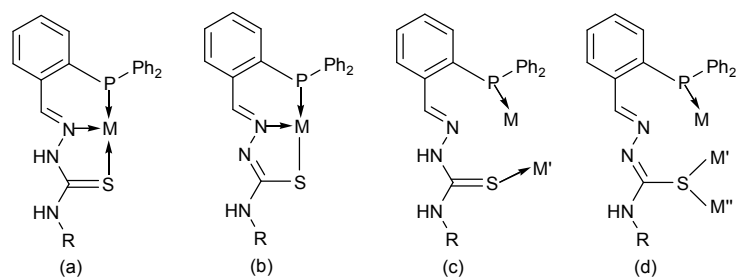


**Table 6** Optimization of reaction conditions for the synthesis of 2-arylbenzazoles catalyzed by ruthenium(II) complexes

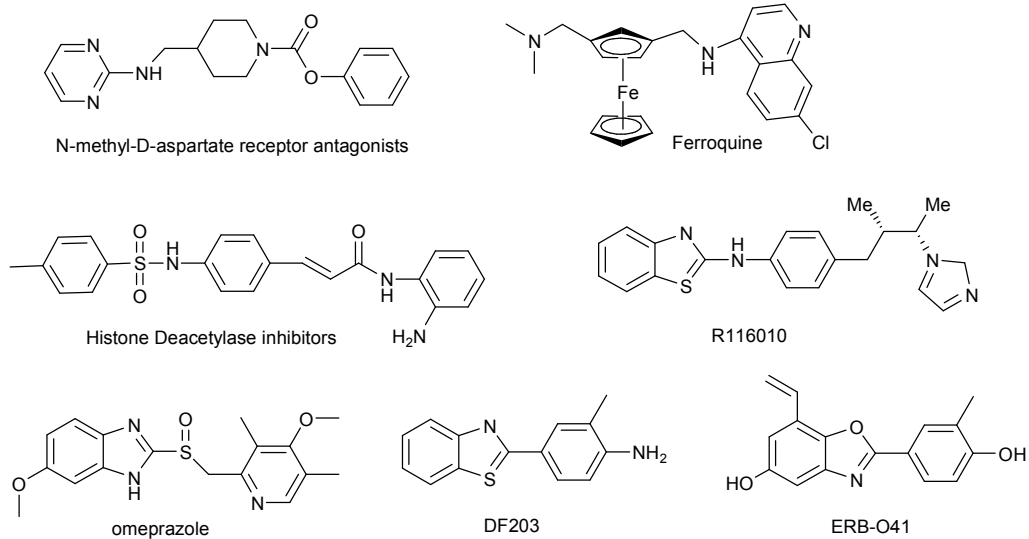
Entry	[Ru]	Terminal substituent's (R)/coligands	Base	Time (h)	Yield (%) <sup>b</sup>
1	-	-	KOH	24	5
2	<b>1</b>	H/PPh <sub>3</sub>	KOH	12	78
3	<b>1</b>	H/PPh <sub>3</sub>	KOH	24	81
4	<b>2</b>	CH <sub>3</sub> /PPh <sub>3</sub>	KOH	12	90
<b>5</b>	<b>2</b>	<b>CH<sub>3</sub>/PPh<sub>3</sub></b>	<b>KOH</b>	<b>24</b>	<b>93</b>
6	<b>2</b>	CH <sub>3</sub> /PPh <sub>3</sub>	KOH	36	93
7	<b>3</b>	C <sub>6</sub> H <sub>5</sub> /PPh <sub>3</sub>	KOH	24	88
8	<b>4</b>	H/AsPh <sub>3</sub>	KOH	24	75
9	<b>5</b>	CH <sub>3</sub> /AsPh <sub>3</sub>	KOH	24	90
10	<b>6</b>	C <sub>6</sub> H <sub>5</sub> /AsPh <sub>3</sub>	KOH	24	82
11	<b>2</b>	CH <sub>3</sub> /PPh <sub>3</sub>	KO <i>t</i> -Bu	24	53
12	<b>2</b>	CH <sub>3</sub> /PPh <sub>3</sub>	NaOH	24	66
13	<b>2</b>	CH <sub>3</sub> /PPh <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	24	7
13	<b>2</b>	CH <sub>3</sub> /PPh <sub>3</sub>	NaHCO <sub>3</sub>	24	11
14	-	-	KOH	24	82 <sup>c</sup>

<sup>a</sup> Reaction conditions: 3.00 mmol of benzyl alcohol, 2.00 mmol of, *o*-phenylenediamine, base (4 mmol), catalyst (0.5 mol %) in 5 mL of toluene at 120 °C. <sup>b</sup>GC-MS yield. Reaction with benzaldehyde (2 mmol)

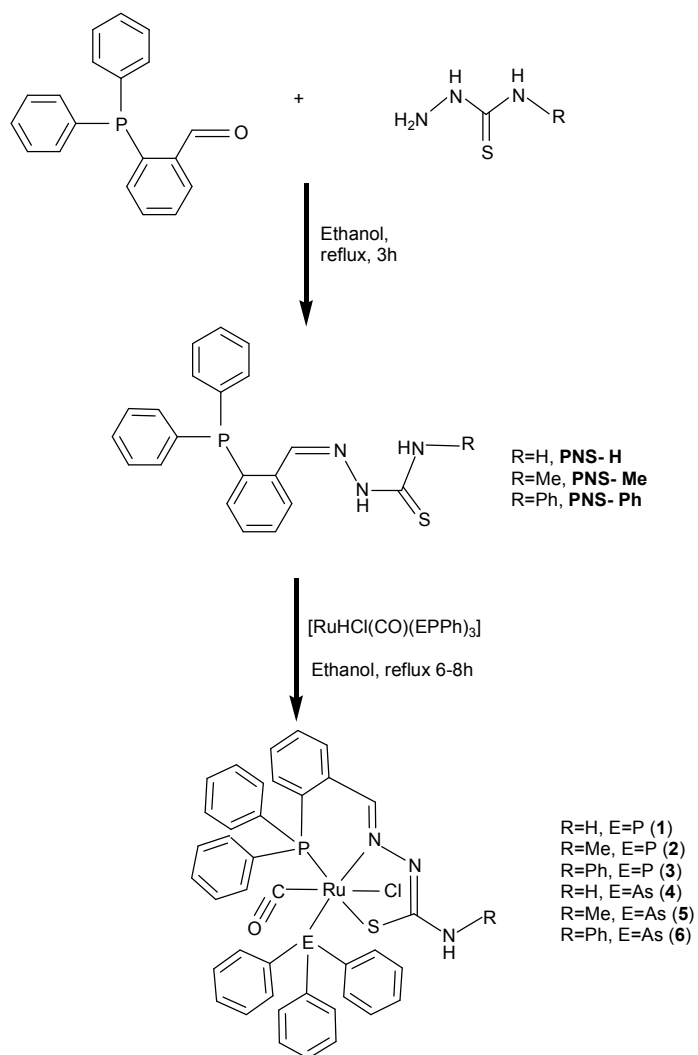
**Table 7** *N*-alkylation of *o*-heterosubstituted aniline with alcohols catalyzed by **2**<sup>a,b</sup>

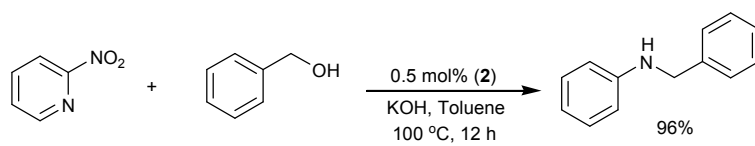


**Scheme 1** Different coordination modes of the triphenyl phosphine-functionalized thiosemicarbazone ligands in various metal complexes.

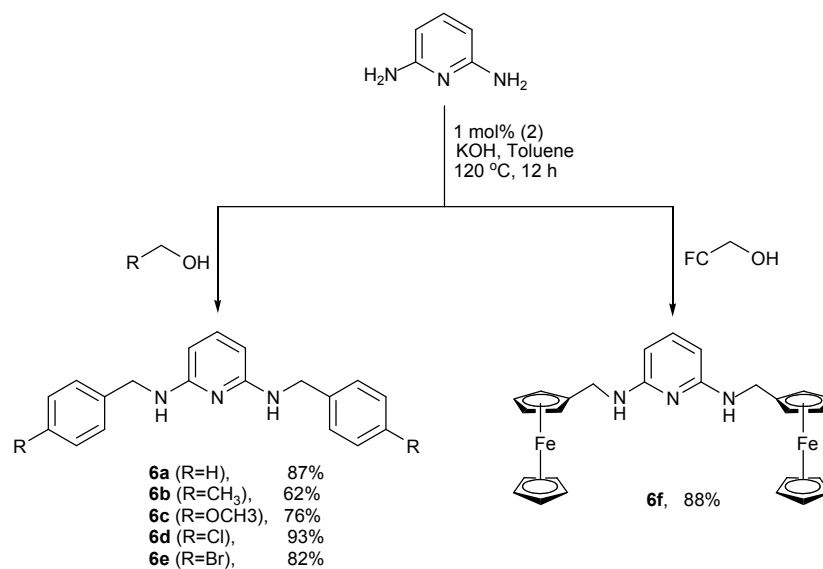


**Scheme 2** Bioactive molecules with pyrimidine, ferrocene, sulfonamide, 2-N-(alkylaminoazole) and benzazole moieties.

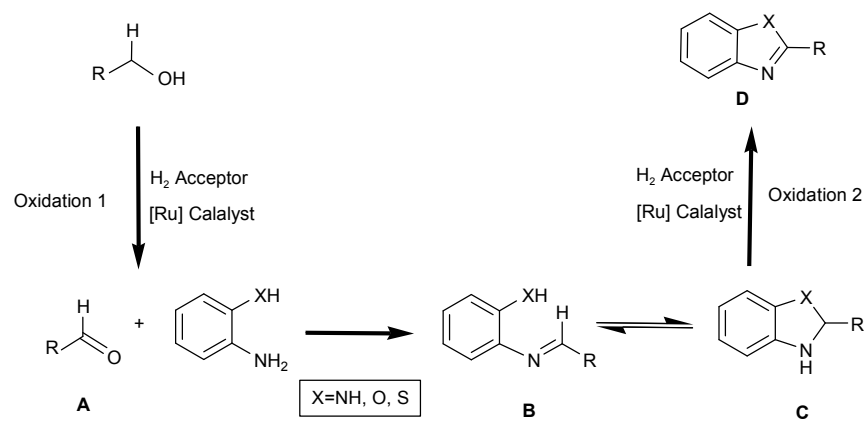
**Scheme 3** Synthesis of the Ruthenium(II) Complexes



**Scheme 4** Direct amination of nitropyridine with benzyl alcohol.

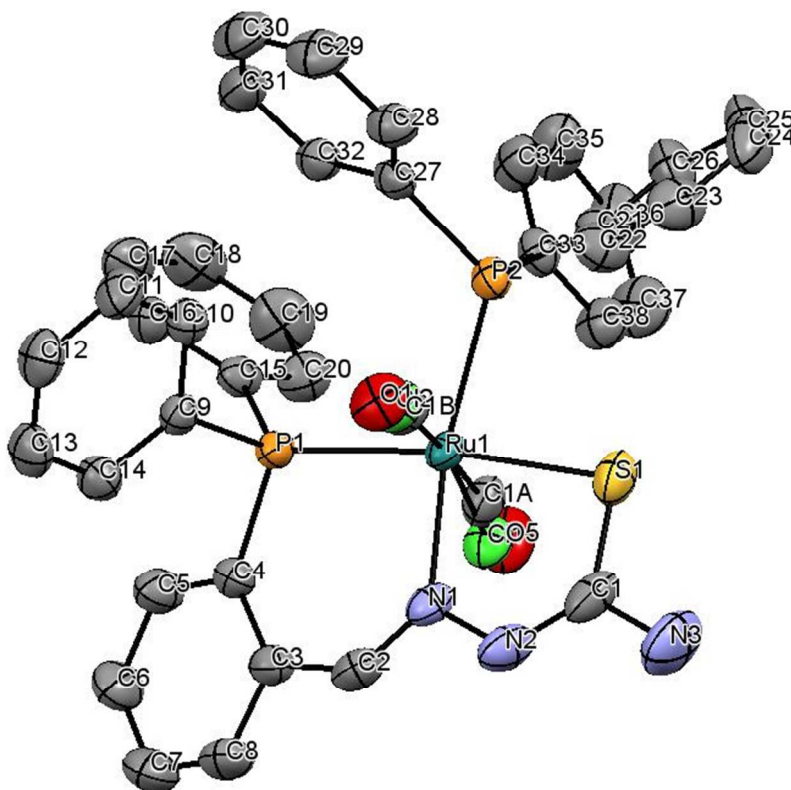
**Scheme 5** Selective *N,N'*-dialkylation of diamine with alcohols catalyzed by **2**<sup>a</sup>

<sup>a</sup> Reaction conditions: 4 mmol of alcohol, 2.00 mmol of diamine, Base (4 mmol), catalyst **2** (1 mol %) in 5 mL of toluene at 120 °C. <sup>b</sup> Isolated yields.

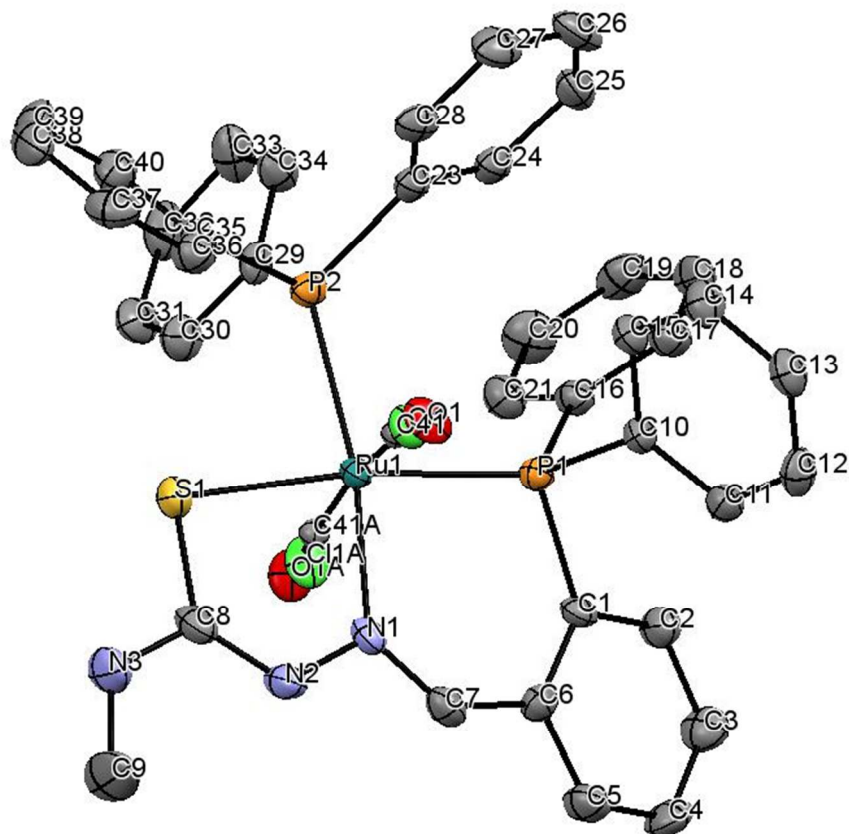


**Scheme 6** Plausible mechanism of ruthenium catalyzed *N*-alkylation of *o*-heterosubstituted anilines.

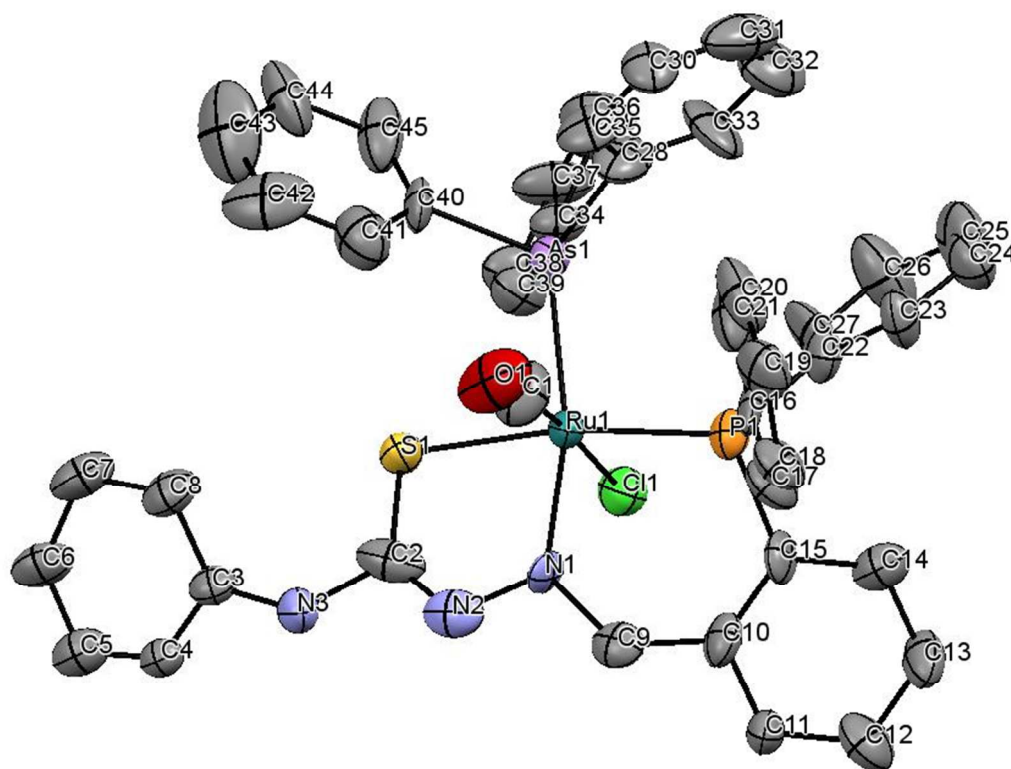




**Figure 1** ORTEP plot of complex  $[\text{RuCl}(\text{CO})(\text{PPh}_3)(\text{PNS-H})]$  (**1**). Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms and solvent are omitted for clarity. Carbonyl and chloride ligands are located in two positions, owing to disorder.



**Figure 2** ORTEP plot of  $[\text{RuCl}(\text{CO})(\text{PPh}_3)(\text{PNS-Me})]$  (**2**). Thermal ellipsoids have been drawn at the 50% probability level and hydrogen atoms are omitted for clarity. Carbonyl and chloride ligands are located in two positions, owing to disorder.



**Figure 3** ORTEP plot of complex  $[\text{RuCl}(\text{CO})(\text{AsPh}_3)(\text{PNS-Ph})]$  (**6**). Thermal ellipsoids have been drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

## Graphical Abstract

A simple, efficient and environmentally benign approach towards *N*-alkylation of heterocyclic amines with alcohols and one-pot synthesis of benzazole derivatives using ruthenium(II) PNS thiosemicarbazone catalyst/KOH (0.5/4 mol %) in toluene.

