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Ruthenium(II) Complexes Containing Phosphine-Functionalized Thiosemicarbazone Ligand: Synthesis, Structures and Catalytic C-N Bond Formation Reactions via N-alkylation

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Abstract

A series of ruthenium(II) complexes incorporating thiosemicarbazone chelate tethered with a diphenylphosphine pendant have been studied. Thus, [(**PNS-Et**)RuCl(CO)(PPh$_3$)] (**1**), [*N,S*-(**PNS-Et**)RuH(CO)(PPh$_3$)$_2$] (**2**) and [(**PNS-Et**)RuCl(PPh$_3$)] (**3**) were synthesized by reactions of various Ru^{II} precursors with 2-(2-(diphenylphosphino)benzylidene)-*N*-ethylthiosemicarbazone **(PNS-Et)**. However, complexation of **PNS-Et** with an equimolar amount of [RuCl$_2$(dmso)$_4$] resulted two different entities [(**PNS-Et**)RuCl(dmso)$_2$] (**4**) and [(**PNS-Et**)$_2$Ru] (**5**) with different structural features in a single reaction. All the Ru^{II} complexes have been characterized by analytical and various spectroscopic techniques. Compounds **1-5** were recrystallized, and the X-ray crystal structures have been reported for **1, 2** and **5**. In the complexes **1** and **3-5** the ligand coordinated in a tridentate monobasic fashion by forming PNS five- and six-membered rings, whereas in **2,** the ligand coordinated in a bidentate monobasic fashion by forming strained NS four-membered ring. Furthermore, compounds **1-5** showed catalytic activity in *N*-alkylation of hetero aromatic amines. Notably, complexes **1-3** were found to be very efficient catalysts toward *N*-alkylation of a wide range of heterocyclic amines with alcohols. In the presence of a catalytic amount of **2** with 50 mol% of KOH, N_1,C_5-dialkylation of 4-phenylthiazol-2-amine has been investigated. Reaction of *in situ* generated aldehyde with amine yields the N_1,C_5-dialkylated products through the hydride ion transformation from alcohol. Complexes **1-3** also catalyzed a variety of coupling reactions of benzyl alcohols and sulfonamides, which were realized, often with 99% isolated yields. Advantageously, only one equivalent of the primary alcohol was consumed in the process.

Key words: Coordination behavior, Phosphino-thiosemicarbazone, Ruthenium(II) complexes, *N*-alkylation, *N,N'*-dialkylation, N_1,C_5-dialkylation.

Introduction

The catalytic construction of C−N bonds via "borrowing hydrogen methodology'' (Scheme 1),[1] also called "hydrogen autotransfer process'',[2] has recently received much attention since nitrogen functionalities occur in various compounds of synthetic and pharmaceutical significance as well as in important biologically active molecules.[3] In contrast with other transition-metal-catalyzed methodologies, for e.g., amination of arylhalides,[4] reductive amination of carbonyl compounds[5] or the hydroamination,[6] and hydroamino-methylation[7] of C−C multiple bonds, etc., the *N*-alkylation of amines/amides with alcohols may serve as a relatively green and environmentally benign alternative since water is the sole byproduct.[8,9] Moreover the use of alcohols as the alkylating agent is direct and simple as the alcohols are readily available, highly stable, low in toxicity, easily stored and handled, low in cost, and relatively high in atom efficiency.

Some of the first homogeneous catalysts for *N*-alkylation reactions were reported in 1981-1985 by Grigg[10] and Watanabe[11], but more recent developments have led to more active catalysts and milder conditions. Beller's group used a dimeric Shvo's ruthenium catalyst system[12] and realized the alkylation of indoles using alcohols, while Williams and co-workers have used ruthenium dimer catalyst[13] to achieve good results. Koten, Milstein and co-workers have obtained good yields in the *N*-alkylation of aromatic amines with diols using 0.1-1 mol % of the PNP pincer type ruthenium catalyst[14,15] at high temperature (130-180 ^{o}C). Also, Yamaguchi and co-workers reported an elegant synthesis of *N*-alkyl substituted amines using readily available $[Cp^*IrCl_2]_2$[16] (1 mol %) at 110 ^{o}C. Kemp also reported that small loadings of [IrCl(PN)COD] afford excellent results in the *N*-alkylation of amines, forming selective mono- and dialkylated products.[17] Two very recently reported compounds of Ru(II)CNN[18] and Ir PNP[19] pincer type catalyst from Matute, Ozawa and co-workers, are the first selective C-N bond formation reaction catalyst for the synthesis of *N*-alkylated amines with excellent results. Our own group has also successful in applying the ruthenium carbonyl complexes[20] to couple a wide range of amines, diamines and alcohols together. Among the aforementioned cases, most of the reported complex catalysts bear ligands containing phosphine coordinating arms usually exhibit much higher catalytic activity due to the steric (bulkiness) and electronic effects (basicity) of the ligand. Unfortunately, such highly active complex catalysts have less been investigated.

Thiosemicarbazones are versatile ligands of considerable attention with respect to their variable coordination behavior and promising biological[21] and catalytic properties.[22] Modifications of the thiosemicarbazone framework, to find new compounds with higher activity and/or to tune their catalytic activity,[22e,f,23] have been extensively studied and relationships between the catalytic activity and chelate formation are evident in a number of cases.[24] Among the most widely studied thiosemicarbazone ligands, a prominent position is occupied by phosphino-thiosemicarbazones,[25] including their terminal alkyl or aryl derivatives.[26-29] With the simultaneous presence of soft and hard donors, the phosphino-thiosemicarbazone ligands exhibit various coordination modes: PNS-tridentate,[25,27] P-S bidentate[28] and P-S bridge in binuclear compounds as well as in oligomers[29] and clusters.[26,29] This makes structural studies more interesting, which are the rational base for structure-activity relationships.

In continuation of our ongoing research in the utility of ruthenium thiosemicarbazone complexes for various organic transformations.[20a,30] In this paper, we report the coordination flexibility of 2-(2-(diphenylphosphino)benzylidene)-*N*-ethylthiosemicarbazone in ruthenium(II) complexes, together with their catalytic properties with regard to *N*-alkylation of amines, diamines and sulphonamides using KOH as the base. The attractive features of these reactions include the use of low toxicity organic materials, excellent atom economy, water is the only by-product, and high selectivity towards the products.

Results and discussion

Synthesis and Characterization of Ruthenium(II) Complexes

The synthetic route to the targeted ligand 2-(2-(diphenylphosphino)benzylidene)-*N*-ethylthiosemicarbazone (**PNS-Et**) are displayed in Scheme 2. First, following the classical methodologies to prepare 2-(diphenylphosphino)benzaldehyde[31] **A-D**, combinations of the 4-ethyl-3-thiosemicarbazide and the accurate 2-(diphenylphosphino)benzaldehyde (**D**) precursor in the presence of acetic acid led to the formation of **PNS-Et** in 96% yield.[29] A series of ruthenium(II) complexes containing **PNS-Et** were synthesized as depicted in Scheme 3. The reactions of the isolated **PNS-Et** with equimolar amounts of [RuHCl(CO)(PPh_3)$_3$], [RuH_2(CO)(PPh_3)$_3$] and [RuCl_2(PPh_3)$_3$] yielded the substituted products **1-3** respectively. However, instead of the expected complex **2a**, ESI-mass spectrometry as well as single crystal

X-ray diffraction study (see below) revealed that an unexpected complex **2** had been formed (Scheme 3). Treatment of **PNS-Et** with an equimolar amount of [$RuCl_2(dmso)_4$] resulted in two different entities **4** and **5** with different structural features in a single reaction (see Scheme 3 for further details). The new complexes are soluble in common organic solvents such as dichloromethane, chloroform, benzene, acetonitrile, ethanol, methanol, dimethylsulfoxide and dimethylformamide. The analytical data of the complexes agreed well with the proposed molecular formulae. The appearance of the $[M\text{-}Cl]^+$ peak in the ESI-MS$^+$ spectra of complexes **1**,**3** and **4** confirms the proposed stoichiometries. However, the molecular ion peak $[M+H]^+$ and $[M]^+$ were identified for complexes **2** and **5**.

Spectroscopic Studies

The IR spectra of the new complexes have been compared with that of the ligand to further elucidate the mode of the ligand coordination. A strong vibration observed at 1583 cm^{-1} in the ligand corresponding to $\nu_{C=N}$ was shifted to 1556−1581 cm^{-1} in the complexes **1** and **3-5** indicating the participation of azomethine nitrogen in bonding.[29] A sharp band observed at 744 cm^{-1}, ascribed to $\nu_{C=S}$ in the ligand, has completely disappeared in the spectra of all the new Ru complexes and the appearance of a new band at 741−749 cm^{-1} due to ν_{C-S} indicated the coordination of the sulfur atom after enolisation followed by deprotonation.[32] The complexes **1, 2** display a medium to strong band in the region 1946−1944 cm^{-1}, which is attributed to the terminally coordinated carbonyl group (C≡O) and is observed at a slightly higher frequency than in the precursor complexes.[33] The Ru–H stretch for **2** could not be observed as an isolated signal, as it falls in the same region of the $\nu_{(C\equiv O)}$ stretch, but it appears as a shoulder (near 1867 cm^{-1}) on the intense $\nu_{(C\equiv O)}$ band. Complex **4** displayed a band at 1092 cm^{-1} characteristic of ν(SO)(S-bonded DMSO) that substantiates the replacement of one O-bonded DMSO and one S-bonded DMSO from the precursor cis-[$RuCl_2(DMSO)_4$] by the ligand, which is in accord with the earlier works.[34] Moreover, the characteristic absorption bands due to PPh_3 were also present in the expected region. The electronic spectra of the complexes (**1-5**) have been recorded in dichloromethane and they displayed four bands in the region around 240−459 nm. The high-energy absorption shoulder in the region 240−328 nm have been assigned to ligand-centered (LC) transitions,[35] the shoulder observed in the region 340−392 nm have been attributed to the ligand to metal charge transfer (LMCT) transitions, and the bands 435−459 nm has been assigned to a forbidden (d→d) transition.

The ^{1}H NMR spectra of the complexes show the signals in the expected regions. The singlets that appeared for the N–NH–C=S proton of the free ligand at 11.53 ppm is absent in the complexes, supporting the enolization and coordination of the thiolate sulfur to the Ru(II) ion (Fig. S4−S6, ESI†). The doublet due to azomethine proton (8.85−8.06 ppm) in the complexes is slightly downfield compared to the free ligand, suggesting deshielding upon coordination to Ru(II) ion. Further, the spectra of all the complexes showed a series of signals for aromatic protons at 7.88−6.55 ppm. The DMSO methyl resonances appear as four singlets between 2.84 and 3.45 ppm, a pattern typical for DMSO coordinated to ruthenium in a *cis* fashion.[36] In addition, a group of peaks appeared around 2.82−0.71 ppm for complexes **1-5** corresponding to the terminal ethyl group protons. In the complex **2**, the hydride signal is clearly observed as a triplet due to coupling with the two magnetically equivalent phosphorus nuclei near –6.75 ppm.[37] The ^{13}C NMR spectra show the expected signals in the appropriate regions. For the uncoordinated ligand, the C=N and C=S signals appear in the regions around 140.25 ppm and 176.62 ppm. Upon coordination and formation of the new Ru complexes, a downfield shift is observed for the signals of the C=N (around 2 ppm), while the C=S carbon atom signals are appeared in the upfield region between 171.80 and 169.78 ppm. This is consistent with the P, N, S coordination and thioenolization of the C=S of thiosemicarbazone moieties. In complexes (**1**−**5**), aromatic carbon atoms of the phenyl group observed around 138.92−125.26 ppm are comparable to the literature values.[29] The C≡O carbon resonating at 206.56−201.12 ppm is comparable with earlier observations.[38] In addition, a couple of signal appeared around 36.27−14.13 ppm for complexes corresponding to the terminal ethyl group carbon.

The presence of a residual PPh_3 coordinated to Ru(II) is confirmed by ^{31}P NMR (Fig. S7−S12, ESI†), where two doublets are observed, respectively at 30.08 ppm (J_{pp} = 22.3 Hz, PPh_3) and 28.31 ppm (J_{pp} = 20.4 Hz, PPh_2) for the complex **1**. These values for coupling constants suggest a cis disposition between the phosphorus nuclei, as already reported for other Ru(II) phosphine complexes.[39] The singlet observed at 48.23 ppm in complex **2**, suggested the presence of two magnetically equivalent triphenylphosphines trans to each other.[40] The ^{31}P NMR spectrum of **3** shows a single resonance at 38.06 ppm, which is shifted by ca. 10 ppm compared to that of **2**. The ^{31}P resonance signals for **4** and **5** are shifted downfield compared to the free ligand, which is typical for the coordination of phosphino-thiosemicarbazone ligand.

Molecular Structures

The structures of complexes **1, 2** and **5** have been established by single crystal X-ray analysis. The details concerning the data collection and structure refinement of the complexes are summarized in Table 1. The molecular structures of **1, 2** and **5** are displayed in Figures **1-3**. The differences in the unit cell packing arrangement of the complexes are shown in Figures **S1-S3** (ESI†). An orange crystal of the complex **1** with approximate dimensions 0.50 x 0.26 x 0.18 mm was isolated and the single crystal X-ray diffraction experiments were carried out at 296(2) K. From the unit cell dimensions, it is clear that the crystal is monoclinic belonging to the $P2_1/c$ space group. 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. The remaining apical coordination sites are filled up by a chlorine atom and carbonyl group. The chloride and carbonyl ligand of the complex is disordered in two orientations, only the major disorder component is shown in Figure 1.

The tridentate **PNS-Et** 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 90.67(7)° [N(1) −Ru(1)−P(1)] and 81.48(7)° [N(1)−Ru(1)−S(1)]. This results in a significant distortion of the {$RuP_2NS(CO)Cl$} core from the ideal octahedral geometry, which is reflected in the twelve *cis* and three *trans* angles. As expected, the PPh_3 ligand occupies mutually *cis* position to PPh_2 head in the thiosemicarbazone chain for better π interaction.[41] The large deviation of the [P(1)−Ru(1)−P(2)] angle [99.33(3)°] from 90 may be ascribed to the steric repulsion between the two adjacent bulky phosphine moieties. The equatorial bond lengths are 2.141(3) [Ru(1)−N(1)], 2.338(8) [Ru(1)−P(1)], 2.383(8) [Ru(1)−S(1)] and 2.389(8) Å [Ru(1)−P(2)]. 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.[42] 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,[29] the related bond distances in [(**PNS-Et**)RuCl(CO)(PPh_3)] (namely, Ru(1)−N(1) = 2.141(3) Å, Ru(1)−P(2) = 2.389(8) Å) follow this rule. The other two axial sites are occupied by a carbonyl group and one chlorine ligand with Ru(1)−C(41A) and Ru(1)−Cl(1A) distance of 1.855(9) and 2.424(2) Å. The CO group occupies the site *trans* to the Cl [C(41A)− Ru(1)−Cl(1A), 171.5(3)°]. This may be a consequence of strong Ru^{II}→CO back donation as indicated by the short Ru−C [1.855(9) Å] bond and low CO stretching frequency (1944 cm^{-1}), which prefers σ or π weak donor groups occupying the site opposite to CO to favor the d−π back donation.

In complex **2**, the ligand [**PNS-Et**] is coordinated to ruthenium as a monoanionic bidentate N,S-donor ligand forming a more strained four-membered chelate ring with a bite angle N(1)−Ru(1)− S(1) of 64.32(8)° (Fig: 2). The formation of such a four-membered chelate ring by the PNS-Et and similar ligands is quite normal.[43] The **PNS-Et** ligand, ruthenium, carbonyl and hydride constitute one equatorial plane of the octahedron with the metal at the center and the two triphenylphosphine ligands take up the remaining two axial positions; hence, they are mutually *trans*. The carbonyl is *trans* to the coordinated nitrogen atom of the thiosemicarbazone and the hydride is *trans* to the sulfur atom. In complexes of ruthenium(II) containing the $Ru(PPh_3)_2$ fragment, the arrangement of PPh_3 ligands ensures optimum π interaction,[41] but in the complexes **2** they are mutually *trans*, probably due to steric reasons as well as the presence of the stronger π acid CO. The Ru(1)–H, Ru(1)–C(1), Ru(1)−P(1) and Ru(1)−P(2) distances are 1.88(4), 1.839(4), 2.3665(10) and 2.3546(11) Å. The observed bond distances are comparable with those found in other reported ruthenium complexes containing PPh_3.[44] Within the Ru(**PNS-Et**) fragment the Ru–N length is comparable to that found in similar four-membered chelates,[43b,c] whereas the Ru–S distance is a little longer than usually observed. The elongation of the Ru–S bond, which is *trans* to the Ru–H bond, may be attributed to the *trans* effect of the hydride ligand. Comparison of the bond lengths in the coordinated thiosemicarbazone ligand with those in the uncoordinated ligand[29] shows that upon coordination the C–S bond has undergone elongation, whereas the adjacent C–N bond has undergone contraction. These changes in bond lengths are consistent with the iminothiolate form of the thiosemicarbazone ligand that appears to be stabilized upon coordination to the metal through loss of the hydrazinic proton. The cis angles P(1)−Ru(1)−S(1) = 88.92(4)°, P(2)−Ru(1)−H = 87.6(12)°, N(1)−Ru(1)−P(1) = 88.64(8)°, N(1)−Ru(1)−P(2) = 88.17(8)° and C(1)−Ru(1)−H = 81.6(13)° are acute, whereas the other cis angles P(1)−Ru(1)−H 90.1(12)°, P(2)−Ru(1)−S(1) = 92.42(4)°, N(1)−Ru(1)−H = 101.4(13)°, C(1)−Ru(1)−S(1) = 112.66(12)°, C(1)−Ru(1)−P(1) = 91.14(12)° and C(1)−Ru(1)−P(2) = 92.21(12)° are obtuse. The trans angles C(9)−Ru(1)−N(2) = 166.4(2)°, P(2)−Ru−P(1) = 178.48(5)° and S(1)−Ru(1)−Cl(1) = 164.23(5)° deviate from linearity. The variations in bond lengths and angles lead to a significant distortion from an ideal octahedral geometry for the complex.

A dark red crystal of the complex **5** with approximate dimensions 0.34 x 0.20 x 0.17 mm was isolated and the single crystal X-ray diffraction experiments were carried out at 295 K. From the unit cell dimensions, it is clear that the crystal is orthorhombic belonging to the $C222_1$ space group. The two **PNS-Et** ligands around the metal centre in **5** are arranged in a *mer–mer* configuration with the two nitrogen atoms *trans* to one another and the two phosphorus and two sulfur atoms in a *cis* configuration (Fig: 3). The average Ru–P, Ru–N and Ru–S bond lengths in **5** are 2.30, 2.06 and 2.38 Å, respectively, which compare well to those observed in related Ru^{II} complexes.[20,41] The average cis angles are S(1)−Ru(1)−S(1) = 85.11(8)°, P(1)−Ru(1)−S(1) = 88.66(5)°, P(1)−Ru(1)−P(1), 97.95(5)°, N(1)−Ru(1)−S(1) = 82.10(9)° and N(1)−Ru(1)−P(1) = 93.34(9)° respectively. The trans angles P(1)−Ru(1)−S(1) = 172.06(5)° and N(1)−Ru(1)−N(1) = 173.40(17)° deviate from linearity. The variations in bond lengths and angles lead to a significant distortion from an ideal octahedral geometry for the complex.

Checking the Factors Involved in the Coordination Behavior of Phosphino-Thiosemicarbazone Ruthenium(II) Complexes

Thiosemicarbazones are versatile ligands and adopt various binding modes with ruthenium ions.[21-35] Based on the previous works those analyzing the factors involved in the coordination behavior of ruthenium with thiosemicarbazones, we remarked on some aspects involving in the formation of these types of compounds. At this time, in the light of the new structures presented in this work, some of the factors previously established for the versatile coordination behavior of ruthenium thiosemicarbazone aggregates must be revised. One of these aspects is related with the deprotonation degree of the thiosemicarbazone ligand, because all of the previous examples clearly indicated that the thiosemicarbazone ligand units involved in the coordination must be deprotonated. It is noteworthy that this basic principle is obeyed by the new structures herein reported (**1-5**). In addition the reported examples indicated that the formation of a five-membered ring is an unusual mode of binding and a four-membered ring is possible. They supported the formation of a four-membered ring as in **2**. A number of reasons have been offered as responsible for their versatility in coordination, such as bulky coligands, bulky diphenylphosphino pendant in thiosemicarbazone and restrict rotation about the N-N bond. These trends have been broken by compounds **1**, **3** and **4** as they were formed using PNS donor atoms of ligand strand. It is concluded that the above mentioned factors are not the only responsible factors in determining the coordination behavior of thiosemicarbazones and there may be some other factors and/ or their collective influence in directing them. There are a number of complexes which reported *trans* configuration of *mer-mer* arrangement. These trends have been broken by complex **5**, and in which *cis* configuration was observed. Another new factor to highlight is that the substitution of ethyl group in the thioamide nitrogen atom of the thiosemicarbazone does not modify the structures formed, but it notably affects the microarchitecture of the crystal structures. Thus, the structures reported herein constitute unique examples of diphenylphosphino-thiosemicarbazone ruthenium(II) complexes, as they exhibit unprecedented arrangements.

Catalysis

Optimization of reaction conditions

Transition-metal 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 recent years.[45] The reaction conditions for this important process are relatively mild and environment friendly. The ruthenium(II) 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 4-methoxybenzyl alcohol in the presence of various bases, and the results are summarized in Table 2. In the absence of base, *N*-alkylation of amine was not observed. The results show the screening of bases as initiators of the catalytic reaction. Weak bases such as Na_2CO_3, K_2CO_3 and Cs_2CO_3 were not effective (Table 2, entries 1−3). However, the use of strong bases such as NaOH, NaO(*t*-Bu), KO(*t*-Bu) and KOH lead to high yields of the desired product (Table 2, entries 4−11). When the reaction was carried out in the presence of KOH, benzothiozol-2-yl-benzylamine was formed in an excellent yield (up to 96%), which we considered to be the choice of the base (Table 2, entry 6). 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 50 mol % of base is needed. The reaction conditions were further optimized through different solvents, the results are given in Table 3. Toluene was found as the best solvent for the *N*-alkylation reaction (Table 3, entry 4). No reaction occurred in the case of water or THF as solvent (Table 3, entries 5, 7), while, 1,4-dioxane, DMF, *o*-xylene, benzene and ethanol resulted in much lower yields (Table 3, entries 1−3, 6 and 8).

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 done to study the influence of the catalyst loadings on the catalytic activity. The results are summarized in Table 4. Catalyst screening in the model reaction revealed that all the ruthenium(II) complexes triggered the reaction, except **5**. Owing to the bischelation of the **PNS-Et** ligands around the metal center in **5**, the lack of a vacant coordination site hinders its catalytic activity. The results also indicate that lower catalyst loadings lead to moderate yields, higher catalyst loadings led to higher yields and higher amine content in the product distribution (Table 4, entries 1−4). Furthermore, considering the results when 0.5 mol % of catalyst was used, it is clear that ruthenium complexes containing hydride species (Table 4, entry 3) lead to higher yields than those containing chlorine as co-ligand (Table 4, entries 1, 2, 4 and 6).

The optimization process led us toward the determination of the best reaction conditions to evaluate the substrate scope. Catalysts **1-3** proved to be the most efficient complexes for the *N*-alkylation of 2-aminobenzothiazole in terms of yield and selectivity and 0.5 mol % catalyst loading was chosen, given the high yields and shorter reaction times needed to complete the process.

Substrate Scope and Limitation

To expand the scope of the present homogeneous catalyst system, the *N*-alkylation reaction has been extended to the copious benzyl alcohol consisting of diverse functional groups. Table 5 summarizes the catalytic activity of **1-3** under the toluene/KOH recipe for this coupling reaction. When an equimolar solutions of *p*-methoxybenzyl alcohol and 2-aminobenzothiazole with 0.5 mol % of **1-3**, the reactions went smoothly to afford the products in 91−98% isolated yield (Table 5, entry 1). The reaction of 2-aminobenzothiazole was carried out with benzyl alcohol to obtain benzothiozol-2-yl-benzylamine in 81−97% yields (Table 5, entries 2). The formation of benzothiozol-2-yl-benzylamine was confirmed by ^{1}H and ^{13}C-NMR spectra, which are given in Figure 4 and 5 as a representative alkylated product. Assignment of signals was further confirmed by DEPT-135 and HSQC-NMR studies (Figure 6 and 7). Benzyl alcohol bearing methyl substituent at *para*-position, still gave coupling products in good yields 76−94% (Table 5, entries 3). The *N*-alkylation with benzyl alcohols bearing a halogen atom at *para* position (Cl or Br) proceeded to give the corresponding products with excellent yields 89−99% (Table 5, entries 4 and 5).

Further, we have extended the present transformation to other heteroaromatic amines such as 2-aminopyrimidine and 2-aminopyridine. These heterocyclic amines also afford good to excellent yields of *N*-alkylated products with alcohols under the optimized conditions. Unsubstituted benzyl alcohol with 2-aminopyrimidine provided the desired products in excellent yield (Table 5, entry 6). *N*-alkylation of benzyl alcohols bearing electron-donating substituents, such as methyl and methoxy, gave the desired products in 84−92% yields (Table 5, entries 7 and 8). Benzyl alcohols bearing a halogen atom, such as chloro and bromo, were proven to be suitable substrates and reactions gave the desired products in 87−97% yields, respectively (Table 5, entries 9 and 10). Similar to the case of 2-aminopyrimidine, the *N*-alkylation of 2-aminopyridine with benzyl alcohol and *p*-Me, *p*-OMe, *p*-Cl, *p*-Br substituted benzyl alcohols, gave the corresponding products (Table 5, entries 11−15) with 74−96 % yields, respectively. The present protocol also performed for *N*-alkylation of aromatic amines such as aminobenzene, 4-methyl, 4-chloro and 4-bromoaniline with ferrocenemethanol in high yield 59−91 % (Table 5, entries 15−18).

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. First 2,6-diaminopyridine was reacted with 4-methoxy benzyl alcohol, which afforded *N*,*N*'-dialkylated product with 70−90 % (Table 5, entry 19). The *N,N'*-dialkylation with benzyl alcohols bearing a halogen atom (Cl or Br) proceeded to give the corresponding products with excellent yields 70−94 % (Table 5, entries 20 and 21). We also tested the alkylation of aliphatic alcohol such as isoamyl alcohol, n-heptanol and cinnamyl alcohol under the optimized reaction conditions. However, these substrates afforded the products in trace amounts. Neither the use of amines that cannot be oxidized to imines gave the desired product (see Supporting Information, Table S1).

The catalytic amine alkylation with ruthenium(II) complexes follows the 'borrowed hydrogen' pathway, extensively studied by Williams, Fujita, Yamaguchi and us.[9-20] 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_2 consumption in this process, however, the reaction benefits from being run in a closed system preventing irreversible H_2 loss.

N_1, C_5-Dialkylation

Having developed a synthetic method for *N*-alkylation of heterocyclic amines, we explored the current concise transformation for dialkylation of 4-phenylthiazol-2-amine (Scheme 4). The earlier optimized conditions were applied to 4-phenylthiazol-2-amine with 4-methoxy benzyl alcohol as alkylating agent, and a mixture of di- and monoalkylated products **A** and **B** was obtained. Under these conditions, the formation of dialkylated product **A** was quite interesting, and no such reports exist in the ruthenium catalysis. Hence, we became interested in investigating the conditions for the selective formation of a single dialkylated product **A**. The identified conditions for this transformation were 4 equiv of 4-methoxy benzyl alcohol, 2 equiv of 4-phenylthiazol-2-amine at 120 °C in toluene, and 24 h of reaction time. These revised optimum conditions were applied to explore the synthesis of N_1,C_5-dialkyl-4-phenylthiazol-2-amines (scheme 5).

The reaction of 4-phenylthiazol-2-amine (1 mmol) with benzyl alcohol (4 mmol) was carried out for 24 h, affording the corresponding N_1,C_5 -dialkylated products with 88% yield. It should be noted that apart from the desired N_1, C_5-dialkylated products, no isomer (the *N*-endo substituted products) and over-alkylated products were observed in all cases. In addition, 1 mol% catalyst was required in all the cases to obtain the products with high yields. These revised optimum conditions were applied to benzyl alcohol bearing *p*-OMe, *p*-Cl group, yields the desired products (82% and 91%). Similarly, reactions of 2-amino-4-(4-chlorophenyl)thiazole with benzyl alcohol afforded the desired product in 93% yield (Scheme 5). The dialkylation of benzyl alcohol bearing an electron-donating methoxy substituent gave the corresponding product 89% yield. The benzyl alcohol bearing an electron-withdrawing substituent (−Cl) was also converted into the corresponding product in 96% yield.

The formation of dialkylated product may be due to the electron-rich nature of five-membered thiazole compared to six membered pyrimidine and pyridine systems. The substitution of phenyl ring at C_4 may further increase the electron density on C_5 of 4-phenylthiazol-2-amine. To confirm this, few experiments were carried out. In the absence of amine, oxidation of 4-methoxybenzyl alcohol to 4-methoxy benzaldehyde was observed under present reaction conditions confirming the dehydrogenation step (Scheme 6a). When the reaction was carried out at low temperature (70 °C) or stopped in-between, imine was observed as major product which confirms the condensation step. We performed the reaction starting from imine (Scheme 6b), under the same reaction conditions, and 76% of dialkylated product was isolated after work-up. Based on the above experimental evidence and previous known hydrogen autotransfer methodologies,[9-20] we propose a possible mechanism for N_1,C_5-Dialkylation of 4-phenylthiazol-2-amine (Scheme 7)**.** Accompanied by the catalytic cycle of ruthenium, the alcohol is first partially dehydrogenated to form the aldehyde **I** with the generation of ruthenium hydride species in the presence of bases, followed by the condensation of the resulting aldehyde with 4-phenylthiazol-2-amine **II** to afford an imine intermediate **III**, which is hydrogenated simultaneously to afford the *N*-alkylated product and the ruthenium hydride species are also consumed. In the presence of ruthenium catalyst, the dehydrogenation of alcohol with simultaneous hydrogenation of imine leads to aldehyde **IA** and *N*-alkylated product **IV**, respectively. Nucleophilic addition of *N*-alkylated product **IV** to aldehyde may form imino alcohol **V**, and its dehydration gives another intermediate **VI.** Subsequent hydrogenation of **VI** provides N_1,C_5**-**dialkylation product **VII** and the ruthenium hydride species are also consumed to complete the catalytic cycle.

N-Alkylation of sulfonamides

N-alkylated sulfonamides constitute an important class of compounds because the sulfonamide moiety is found in a large number of agrochemicals and pharmaceuticals.[46] The most commonly used methods for the synthesis of sulfonamides include the condensation of amines with sulfonyl chlorides,[47] reductive amination of sulfonamides with alkyl halides[48] and the reaction of activated sulfonate esters with amines.[49] Most of these methods are associated with the limitations such as poor selectivity, side reactions, tedious work-up procedures and the generation of unwanted inorganic salts. Alternatively, few reports are also available on the synthesis of *N*-alkylated sulfonamides directly from alcohols. Recently, Ru/diphosphine,[50] Ru/Fe_3O_4[51] and Cu[52] have been applied for the synthesis of *N*-alkylated sulfonamides directly from benzyl alcohols.

Inspired by the above interesting result, we envisioned that ruthenium based catalysts may be also suitable for the synthesis of amides through the dehydrogenation-condensation-hydrogenation sequence (so called borrowing hydrogen methodology). Although, the reaction conditions were similar as for the *N*-alkylation of heterocyclic amines, however, reaction took at slightly higher temperature. In order to explore the scope of the present method, the reactions of copious sulfonamides were successfully performed with a variety of alcohols. As shown in Table 6, substituted groups on the aromatic ring had no negative influence on the alkylation reactions and the corresponding secondary sulfonamides were produced in 82–99 % isolated yields (Table 6, entries 1–5). By comparing the *N*-alkylation reactions of *p*-toluenesulfonamide, *p*-chlorobenzenesulfonamide and benzenesulfonamide, it is clear that electron-rich as well as electron poor groups were well tolerated. In addition, the coupling reaction of *p*-toluenesulfonamide with cyclohexyl alcohol gave the corresponding product in moderate yield (62–74 %, Table 6, entry 6), however, low yield (21–54 %) were obtained by the reactions of methanesulfonamide with benzyl alcohol (Table 6, entry 7).

Conclusion

We have reported the synthesis and characterization of a series of ruthenium complexes bearing 2-(2-(diphenylphosphino)benzylidene)-*N*-ethylthiosemicarbazone (**PNS-Et**) ligands. Typically, [(**PNS-Et**)RuCl(CO)(PPh$_3$)] (**1**), [*N,S*-(**PNS-Et**)RuH(CO)(PPh$_3$)$_2$] (**2**) and [(**PNS-Et**)RuCl(PPh$_3$)$_2$] (**3**) were synthesized by reactions of various Ru^{II} precursors with deprotonated **PNS-Et**. Complexation of **PNS-Et** with an equimolar amount of [RuCl$_2$(dmso)$_4$] resulted two different entities [(**PNS-Et**)RuCl(dmso)$_2$] (**4**) and [(**PNS-Et**)$_2$Ru] (**5**) with different structural features in a single reaction. The structures of these complexes were unambiguously determined by spectroscopic methods and X-ray single crystal analysis (**1, 2** and **5**). It is interesting to note that one of the complexes obtained (**2**) has thiosemicarbazone coordinated as NS through the hydrazinic nitrogen and thiolate sulfur by forming four-membered ring, whereas in other complexes, the same ligand coordinated as PNS monobasic tridentate donor. The catalytic study of complexes **1−5** towards amine *N*-alkylation reactions was completed, showing that all catalysts are active toward catalytic transformations. In the *N*-alkylation process, the complexes **1−3** have been proven to be efficient catalysts under mild conditions in comparison to its analogues and other ruthenium and iridium complexes.[53] Also, **1−3** have shown high tolerance to functional groups in the hetero (aromatic) amine and benzyl alcohol moieties, however, some limitations for aliphatic alcohols. Furthermore, selective *N,N'*-dialkylation occurred when hetero aromatic diamines were subjected to the reaction conditions. Reaction of 4-phenylthiazol-2-amines with benzyl alcohols gave N_1,C_5-dibenzyl-4-phenylthiazol-2-amines in good yields in the presence of KOH. On the other hand, **1−3** have been proven to be very efficient catalysts in the *N*-alkylation of a wide variety of sulfonamides and alcohols. From synthetic point of view, the protocol is highly attractive because of easily available starting materials, high atom efficiency, broad substrate scope, water as only byproduct and environmental friendliness. Further studies to explore new potential of alcohols as electrophiles are under way.

Experimental section

General Procedures

Unless otherwise noted, all reactions were performed under an atmosphere of air. Thin-layer chromatography (TLC) was carried out on Merck 1.055 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 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, N and S 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. The electronic spectra of the complexes were performed on a Shimadzu UV−1650 PC spectrophotometer using dichloromethane as the solvent. 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. 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, triphenylphosphine 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,[31] $[RuHCl(CO)(PPh_3)_3]$,[54] $[RuH_2(CO)(PPh_3)_3]$,[55] $[RuCl_2(PPh_3)_3]$[56] and $[RuCl_2(dmso)_4]$.[57]

2-(2-(diphenylphosphino)benzylidene)-*N*-ethylthiosemicarbazone (PNS-Et):

To a solution of 2-(diphenylphosphino)benzaldehyde (1 g, 3.4 mmol) and 4-ethyl-3-thiosemicarbazide (0.42 g, 3.4 mmol) in ethanol (30 mL) were added 2−3 drops of glacial acetic acid. The pale yellow solution was heated under reflux over a 2 h period, and then concentrated to dryness. The resulting yellow oil was treated with diethyl ether (2 x 10 mL). The pale yellow precipitate was filtered off, washed with diethyl ether (10 mL) and dried under *vacuo.* Yield: 96% (1.62 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, 3120 (m, ν_{NH}); 1584 + 1478 (s, $\nu_{C=N}$ + ν_{C-N}); 744 (s, $\nu_{C=S}$). UV-Vis (CH_2Cl_2), λ_{max} (nm): 297, 332, 353. ^{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 −10.81. ESI-MS: *m*/*z* = 391.01 $[M+H]^+$.

[(PNS-Et)RuCl(CO)(PPh$_3$)] (1):

A suspension of $[RuHCl(CO)(PPh_3)_3]$ (0.5 g, 0.52 mmol) in ethanol (40 mL) was treated with **PNS-Et** (0.2 g, 0.52 mmol) and the mixture was gently refluxed for 8h. During this time the color changed to orange. The solvent was reduced to half of the volume on a rotary evaporator, and the suspension was filtered, washed thoroughly with cold ethanol (10 mL) and diethyl ether (2 x 20 mL). The product was finally dried under vacuum, affording an orange solid in 79% (0.33 g) yield. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated solution of **1** in CH_2Cl_2/C_2H_5OH. Mp: 258 °C. Anal. Calcd for $C_{41}H_{36}ClN_3OP_2RuS$: C, 60.25; H, 4.44; N, 5.14; S, 3.92%. Found: C, 60.49; H, 4.14; N, 5.36; S, 4.02%. IR (KBr disks, cm^{-1}): 3412, 3050 (m, ν_{NH}); 1944 (s, $\nu_{C\equiv O}$); 1582 + 1480 (s, $\nu_{C=N}$ + ν_{C-N}); 747 (s, ν_{C-S}); 1432, 1091, 695 (s, for PPh$_3$). UV-Vis (CH_2Cl_2), λ_{max} (nm): 258, 283, 358, 440. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.12 (t, 3H, *J* = 7 Hz, $-CH_3$), 2.46−2.53 (m, 2H, $-CH_2$), 6.58 (td, 2H, *J* = 7, 1.6 Hz, Ar H), 6.70 (t, 1H, *J* = 8.8 Hz, Ar H), 6.89 (t, 2H, *J* = 7.2 Hz, Ar H), 7.12 (td, 2H, *J* = 6.0, 2.0 Hz, Ar H), 7.20−7.28 (m, 3H, Ar H), 7.35−7.42 (m, 3H, Ar H), 7.44 (td, 3H, *J* = 8.0, 1.6 Hz, Ar H), 7.49−7.63 (m, 8H, Ar H), 7.74 (d, 4H, *J* = 8.0 Hz, Ar H), 7.85−7.88 (m, 1H, Ar H), 8.42 (s, 1H, $-NH_{terminal}$), 8.85 (d, IH, *J* = 4.8 Hz, −CH=N). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 14.24 ($-CH_3$), 24.5 ($-CH_2$), 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), 139.96 (−CH=N), 170.14 (C=S), 206.56 (C≡O). ^{31}P NMR (162 MHz, DMSO-d$_6$): δ 30.08 (d, *J* = 22.3 Hz, PPh$_3$), 28.31 (d, *J* = 20.4 Hz, PPh$_2$). ESI-MS: *m*/*z* = 781.57 [M–Cl]$^+$.

[*N*,*S*-(PNS-Et)RuH(CO)(PPh$_3$)$_2$] (2)

A suspension of [RuH$_2$(CO)(PPh$_3$)$_3$] (0.2 g, 0.22 mmol) in CH$_2$Cl$_2$ (20 mL) was treated with **PNS-Et** (0.086 g, 0.22 mmol) in ethanol (20 mL) and the mixture was gently refluxed for 12 h. During this time the color changed to green. 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 vacuum, affording a green solid in 75 % (0.13 g) yield. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated solution of **2** in CH$_2$Cl$_2$/C$_2$H$_5$OH. Mp: 234 °C. Anal. Calcd for $C_{59}H_{52}N_3OP_3RuS$: C, 67.80; H, 5.02; N, 4.02; S, 3.07%. Found: C, 67.95; H, 5.12; N, 4.14; S, 3.16%. IR (KBr disks, cm^{-1}): 3414, 3051 (m, ν_{NH}); 1946 (s, $\nu_{C\equiv\equiv O}$); 1867 (w, $\nu_{Ru\text{-}H}$) 1583 + 1498 (s, $\nu_{C=N} + \nu_{C-N}$); 741 (s, ν_{C-S}); 1432, 1074, 693 (s, for PPh$_3$). UV-Vis (CH$_2$Cl$_2$), λ_{max} (nm): 261, 293, 392, 435. ^{1}H NMR (400 MHz, CDCl$_3$): δ −6.75 (t, 1H, *J* = 19.1 Hz, RuH), 0.71 (t, 3H, *J* = 7.2 Hz, $-CH_3$), 2.70−2.77 (m, 2H, $-CH_2$), 6.78 (t, 1H, *J* = 4 Hz, Ar H), 6.99−7.05 (m, 3H, Ar H), 7.08 (td, 2H, *J* = 5.9, 1.4 Hz, Ar H), 7.14 (td, 2H, *J* = 5.0 Hz, Ar H), 7.18−7.39 (m, 21H, Ar H), 7.44 (t, 2H, *J* = 7.5 Hz, Ar H), 7.58−7.62 (m, 13H, Ar H), 7.90 (s, 1H, $-NH_{terminal}$), 8.06 (d, IH, *J* = 3.6 Hz, −CH=N). ^{13}NMR (100 MHz, CDCl$_3$): δ 14.39 ($-CH_3$), 36.27 ($-CH_2$), 127.32 (Ar C), 127.98 (Ar C), 128.40 (Ar C), 128.45 (Ar C), 128.57 (Ar C), 128.91 (Ar C), 129.34 (Ar C), 129.85 (Ar C), 130.64 (Ar C), 131.41 (Ar C), 131.93 (Ar C), 131.95 (Ar C), 132.01 (Ar C), 132.10 (Ar C), 132.15 (Ar C), 132.63 (Ar C), 133.62 (Ar C), 133.82 (Ar C), 134.56 (Ar C), 135.03 (Ar C), 135.18 (Ar C), 135.39 (Ar C), 135.59 (Ar C), 138.29 (Ar C),138.43 (Ar C), 138.92 (Ar C), 140.29 (−CH=N), 170.21 (C=S), 201.12 (C≡O). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.67 (PPh_2), 48.23 (s, PPh_3). ESI-MS: *m*/*z* = 1046.21 $[M+H]^+$.

[(PNS-Et)RuCl(PPh$_3$)] (3)

A suspension of $[RuCl_2(PPh_3)_3]$ (0.2 g, 0.207 mmol) in CH_2Cl_2 (40 mL) was treated with **PNS-Et** (0.081 g, 0.207 mmol) in ethanol and the mixture was gently refluxed for 8 h. During this time the color changed to red. 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 vacuum, affording a red solid in 82 % (0.18 g) yield. Mp: 245 °C. Anal. Calcd for $C_{40}H_{36}ClN_3P_2RuS$: C, 60.87; H, 4.60; N, 5.32; S, 4.06%. Found: C, 60.61; H, 4.16; N, 5.14; S, 4.26%. IR (KBr disks, cm^{-1}): 3401, 3051 (m, ν_{NH}); 1556 + 1522, 1481 (s, $\nu_{C=N}$ + ν_{C-N}); 746 (s, ν_{C-S}); 1433, 1089, 694 (s, for PPh_3). UV-Vis (CH_2Cl_2), λ_{max} (nm): 247, 340, 459. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.12 (t, 3H, *J* = 7 Hz, $-CH_3$), 2.72−2.82 (m, 2H, $-CH_2$), 6.70 (t, 1H, *J* = 8.8 Hz, Ar H), 7.04 (t, 1H, *J* = 8.1 Hz, Ar H), 7.09 (t, 2H, *J* = 8.9 Hz, Ar H), 7.15 (t, 4H, *J* = 7.2 Hz, Ar H), 7.19−7.25 (m, 5H, Ar H), 7.33 (td, 2H, *J* = 6.0, 1.7 Hz, Ar H), 7.38−7.41 (m, 1H, Ar H), 7.47 (td, 3H, *J* = 8.3, 1.9 Hz, Ar H), 7.73−7.52 (m, 8H, Ar H), 7.80−7.88 (m, 4H, Ar H), 8.11 (s, 1H, $-NH_{terminal}$), 8.52 (d, IH, *J* = 8.1 Hz, −CH=N). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 14.14 ($-CH_3$), 36.12 ($-CH_2$), 127.41 (Ar C), 128.31 (Ar C), 128.66 (Ar C), 128.70 (Ar C), 128.77 (Ar C), 128.96 (Ar C), 131.39 (Ar C), 131.49 (Ar C), 131.99 (Ar C), 132.02 (Ar C), 133.10 (Ar C), 133.30 (Ar C), 133.74 (Ar C), 133.82 (Ar C), 136.42 (Ar C), 136.64 (Ar C), 140.04 (−CH=N), 169.78 (C-S). ^{31}P NMR (162 MHz, DMSO-d$_6$): δ 26.23 (s, PPh_2), 38.06 (s, PPh_3). ESI-MS: *m*/*z* = 753.82 $[M–Cl]^+$.

[(PNS-Et)RuCl(dmso)$_2$] (4) and [(PNS-Et)$_2$Ru] (5)

A suspension of $[RuCl_2(dmso)_4]$ (0.2 g, 0.44 mmol) in CH_2Cl_2 (40 mL) was treated with **PNS-Et** (0.172 g, 0.44 mmol) in ethanol and the mixture was gently refluxed for 12 h. During this time the color changed to dark red. The solvent was removed on a rotary evaporator. The residue was then chromatographed on alumina oxide with ethyl acetate/ diethyl ether. A light brown band was eluted with 2:8 ethyl acetate/diethyl ether mixtures and it was identified as **4** (yield 0.132 g, 43%). A brownish yellow band was eluted with 6:4 ethyl acetate/diethyl ether mixture and it was identified as **5** (yield 0.105 g, 27%). Single crystals of **5** were obtained by slow diffusion of diethyl ether into a saturated solution of the complex in ethyl acetate. Complex **4:** Mp: 273 °C.

Anal. Calcd for $C_{26}H_{33}ClN_3OP_2RuS_3$: C, 45.70; H, 4.87; N, 6.15; S, 14.08%. Found: C, 45.92; H, 4.78; N, 6.05; S, 14.26%. IR (KBr disks, cm^{-1}): 3430, 320 (m, ν_{NH}); 1572 + 1482 (s, $\nu_{C=N}$ + ν_{C-N}); 749 (s, ν_{C-S}); 1092 (s, for S-bonded dmso). UV-Vis (CH_2Cl_2), λ_{max} (nm): 254, 309, 356, 427. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.10 (t, 3H, *J* = 7 Hz, −CH_3), 2.46−2.74 (m, 2H, −CH_2), 2.84−3.45 (s, 12H, dmso), 6.55 (t, 2H, *J* = 8.0 Hz, Ar H), 6.55 (t, 2H, *J* = 8.0 Hz, Ar H), 6.72 (t, 1H, *J* = 7.6 Hz, Ar H), 6.89−6.86 (m, 1H, Ar H), 7.63−7.10 (m, 8H, Ar H), 7.91 (s, 1H, $NH_{terminal}$), 8.41 (d, 1H, *J* = 8.1 Hz, −CH=N). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 14.18 (−CH_3), 24.21 (dmso), 34.12 (−CH_2), 125.26 (Ar C), 125.55 (Ar C), 127.44 (Ar C), 128.01 (Ar C), 128.78 (Ar C), 128.85 (Ar C), 129.01 (Ar C), 129.12 (Ar C), 129.87 (Ar C), 132.94 (Ar C), 133.36 (Ar C), 133.56 (Ar C), 135.60 (Ar C), 135.70 (Ar C), 136.05 (Ar C), 136.24 (Ar C), 137.24 (Ar C), 137.43 (Ar C), 138.82 (Ar C), 138.91 (Ar C), 140.13 (−CH=N), 170.12 (C−S). ^{31}P NMR (162 MHz, DMSO-d$_6$): δ 28.78 (s, PPh_2). ESI-MS: *m*/*z* = 662.57 [M–Cl]$^+$. Complex **5**: Mp: 285 °C. Anal. Calcd for $C_{44}H_{42}N_6P_2RuS_2$: C, 59.92; H, 4.80; N, 9.53; S, 7.27%. Found: C, 60.25; H, 4.56; N, 9.24; S, 7.38%. IR (KBr disks, cm^{-1}): 3432, 3208 (m, ν_{NH}); 1579 + 1481 (s, $\nu_{C=N}$ + ν_{C-N}); 749 (s, ν_{C-S}). UV-Vis (CH_2Cl_2), λ_{max} (nm): 240, 328, 435. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.05 (t, 6H, *J* = 7 Hz, −CH_3), 2.42−2.63 (m, 4H, −CH_2), 6.57 (m, 4H, *J* = 7.2 Hz, Ar H), 6.70 (t, 2H, *J* = 8.8 Hz, Ar H), 6.89 (t, 6H, *J* = 7.2 Hz, Ar H), 7.75−7.02 (m, 14H, Ar H), 7.86 (t, 2H, *J* = 7.2 Hz, Ar H), 8.11 (s, 2H, −$NH_{terminal}$), 8.46 (d, 2H, *J* = 8.3 Hz, −CH=N). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 14.13 (−CH_3), 30.60 (−CH_2), 128.00 (Ar C), 128.10 (Ar C), 128.41 (Ar C), 128.64 (Ar C), 129.06 (Ar C), 129.89 (Ar C), 130.32 (Ar C), 130.48 (Ar C), 131.03 (Ar C), 131.29 (Ar C), 131.38 (Ar C), 131.68 (Ar C), 131.79 (Ar C), 132.80 (Ar C), 132.91 (Ar C), 133.12 (Ar C), 133.54 (Ar C), 133.79 (Ar C), 133.90 (Ar C), 134.00 (Ar C), 138.91 (C=N), 171.80 (C−S). ^{31}P NMR (162 MHz, DMSO-d$_6$): δ 29.12 (s, PPh_2). ESI-MS: *m*/*z* = 881.84 [M]$^+$.

Catalysis

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

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

Representative spectral data for *N*-Benzylbenzo[d]thiazol-2-amine: ^1H NMR (400MHz, $CDCl_3$): 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.

Typical procedure for N_1, C_5-Dialkylation of amines with alcohols

In a 25 mL round bottomed flask were placed 1 mol % of ruthenium(II) catalyst, 4 mmol of benzyl alcohol, 2 mmol of 4-phenylthiazol-2-amine, 50 mol % of KOH and 2.0 mL of toluene. The reaction flask was heated at 120 °C for 24 h in an oil bath. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H_2O (3 mL) was added and the organic layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with magnesium sulfate and concentrated. The crude product was purified by column chromatography (ethyl acetate/dichloromethane). Reported isolated yields are an average of two runs.

Typical procedure for *N*-alkylation of sulfonamides with alcohols

In a 25 mL round bottomed flask were placed 0.5 mol % of ruthenium(II) catalyst, 2 mmol of benzyl alcohol, 2 mmol of sulfonamide, 50 mol % of KOH and 2 mL of toluene. The reaction flask was heated at 120 °C for 12 h in an oil bath. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H_2O (3 mL) was added and the organic layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with magnesium sulfate and concentrated. The crude product was purified by column chromatography (ethyl acetate/hexane). Reported isolated yields are an average of two runs.

The catalytic reactions given in Tables 2−6 were similarly conducted. The resulting amines and amides were identified by comparison of the ^1H and ^{13}C NMR data with those previously reported (S16−S28, ESI†).

X-ray Crystallographic Study

Crystals of **1, 2** and **5** were mounted on glass fibers and used for data collection. Crystal data were collected at 296(2) K(**1**) and 295(2) K (**2** and **5**) using a Gemini A Ultra Oxford Diffraction automatic diffractometer. Graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) was used throughout. The absorption corrections were performed by the multi-scan method. Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods using the program SHELXS.[58] Refinement and all further calculations were carried out using SHELXL.[58] 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 of complex **1**, 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 **5** and a better data set, only poor-quality data were obtained.

Acknowledgment

The authors are grateful to Indian Institute of Technology, Chennai, Indian Institute of Science, Bangalore and Punjab University, Chandigarh, for providing instrumental facilities.

Electronic supplementary information (ESI) available:

The unit cell packing diagram for complexes **1, 2** and **5** (Fig. S1-S3), representative NMR (^{1}H and ^{31}P) spectra of ligand and complexes, detailed experimental procedures and spectral data for *N*-alkylated products. CCDC reference numbers 1021256, 1021259 and 1021258 for complexes **1, 2** and **5**. For ESI and crystallographic data in CIF or other electronic format see DOI:

References

1. (a) M. H. S. A. Hamid, P. A. Slatford and J. M. J. Williams, *Adv. Synth. Catal.* **2007**, 349, 1555. (b) G. W. Lamb and J. M. J. Williams, *Chimica Oggi* 2008, **26**, 17−19; (c) T. D. Nixon, M. K. Whittlesey and J. M. J. Williams, *Dalton Trans.* 2009, 753−762.
2. (a) G. Guillena, D. J. Ramon and M. Yus, *Chem. Rev.* 2010, 110, 1611−1641; (b) A. Martinez-Asencio, D. J. Ramon and M. Yus, *Tetrahedron* 2011, **67**, 3140−3149; (c) A. Martinez-Asencio, M. Yus and D. J. Ramon, *Synthesis*, 2011, 3730−3740.
3. (a) S. A. Lawerencem, *Amines: Synthesis Properties and Applications;* Cambridge University: Cambridge, 2004; (b) K. P. C. Vollhardt and N. E. Schore, *Organic Chemistry: Structure and Function,* 5th ed., W H. Freeman: New York, 1999; (c) Comprehensive Heterocyclic Chemistry, (Eds.: A.R. Katritzky and C. W. Rees), Elsevier, Oxford, 1996; (d) P. Lechat, S. Tesleff and W. C. Bownan, *Aminopyridines and Similarly Acting Drugs,* Pergamon Press, Oxford, 1982.
4. (a) R. J. Lundgren, M. Stradiotto, *Aldrichim. Acta* 2012, **45**, 59−65; (b) D. S. Surry and S. L. Buchwald, *Chem. Sci.* 2010, **1**, 13−31; (b) F. Monnier, M. Taillefer, *Angew. Chem., Int. Ed.* 2008, **47**, 3096−3099.
5. (a) C. F. Lane, *Synthesis* 1975, 135–146; (b) G. W. Gribble, *Chem. Soc. Rev*. 1998, **27**, 395–404; (c) A. F. Abdel-Magid, K. G. Carson, B. D. Harris, C. A. Maryanoff and R. D. Shah, *J. Org. Chem*. 1996, **61**, 3849–3862.
6. (a) R. Severin and S. Doye, *Chem. Soc. Rev.* 2007, **36**, 1407–1420; (b) M. Beller, C. Breindl, M. Eichberger, C. G. Hartung, J. Seayad, O. Thiel, A. Tillack and H. Trauthwein, *Synlett* 2002, 1579–1594.
7. (a) K.-S. Miller, F. Koc, S. Ricken and P. Eilbracht, *Org. Biomol. Chem.* 2006, **4**, 826–835; (b) L. Routaboul, C. Buch, H. Klein, R. Jackstell and M. Beller, *Tetrahedron Lett.* 2005, **46**, 7401–7405.
8. For a selected reviews on Borrowing Hydrogen, see: (a) T. Suzuki, *Chem. Rev*., 2011, **111**, 1825–1845; (b) R. H. Crabtree *Organometallics*, 2011, **30**, 17–19; (c) G. E. Dobereiner and R. H. Crabtree, *Chem. Rev*., 2010, **110**, 681–703;

9. For selected examples, see: (a) F. Li, H. Shan, L. Chen, Q. Kang and Zou, P. *Chem. Commun*., 2012, **48**, 603–605; (b) S. Bahn, S. Imm, L. Neubert, M. Zhang, H. Neumann

and M. Beller, *Chem. Eur. J.* 2011,**17**, 4705–4708; (c) M. Zhang, S. Imm, S. Bahn, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2011, **50**, 11197–11201; (d) O. Saidi, A. J. Blacker, M. M. Farah, S. P. Marsden and J. M. J. Williams, *Chem. Commun.*, 2010, **46**, 1541–1543; (e) R. Kawahara, K. Fujita and R. Yamaguchi, *J. Am. Chem. Soc.*, 2010, **132**, 15108–15111; (f) C.-F. Chang, Fu, Y.-H. Liu, S.-M. Peng, J.-T. Chen and S.-T. Liu, *Dalton Trans.*, 2009, 861–867; (g) A. P. Da Costa, M. Sanau, E. Peris and B. Royo, *Dalton Trans.*, 2009, 6960–6966; (h) O. Saidi, A. J. Blacker, M. M. Farah, S. P. Marsden and J. M. J. Williams, *Angew. Chem., Int. Ed.*, 2009, **48**, 7375–7378.

10. R. Grigg, T. R. B, Mitchell, S. Sutthivaiyakit, N. Tongpenyai, *J. Chem. Soc., Chem. Commun.* 1981, **12**, 611–612.

11. (a) Y. Tsuji, H.-T. Huh and Y. Ohsugi, Y. Watanabe, *J. Org. Chem.* 1985, **50**, 1365–1370; (b) Y. Watanabe, Y. Tsuji, Y. Ohsugi and T. Ohta, *J. Org. Chem.* 1984, **49**, 3359–3363; (c) Y. Watanabe, Y. Tsuji and Y. Ohsugi, *Tetrahedron Lett.* 1981, **22**, 2667 – 2670.
12. (a) D. Hollmann, S. Bahn, A. Tillack and M. Beller, *Chem. Commun*. 2008, 3199–3201; (b) S. Bahn, D. Hollmann, A. Tillack and M. Beller, *Adv. Synth. Catal.* 2008, **350**, 2099–2103; (c) D. Hollmann, S. Bahn, A. Tillack, R. Parton, R. Altink and M. Beller, *Tetrahedron Lett*. 2008, **49**, 5742–5745; (d) D. Hollmann, S. Bahn, A. Tillack and M. Beller, *Angew. Chem.* 2007, **119**, 8440–8444.
13. (a) M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson and J. M. J. Williams, *J. Am. Chem. Soc.* 2009, **131**, 1766–1774; (b) M. H. S. A. Hamid and J. M. Williams, *Chem. Commun.* 2007, 725–727.
14. R. A. T. M. Abbenhuis, J. Boersma and G. V. Koten, *J. Org. Chem.* 1998, **63**, 4282–4290.
15. C. Gunanathan and D. Milstein, *Angew. Chem., Int. Ed.* 2008, **47**, 8661–8664.
16. K. Fujita, Y. Enoki and R. Yamaguchi, *Tetrahedron* 2008, **64**, 1943–1954.
17. (a) B. Blank, S. Michlik, R. Kempe, *Adv. Synth. Catal.* 2009, **351**, 2903–2911; (b) B. Blank, S. Michlik, and R. Kempe, *Chem. Eur. J.* 2009, **15**, 3790–3799; (c) B. Blank, M. Madalska and R. Kempe, *Adv. Synth. Catal.* 2008, **350**, 749–758.
18. S. Agrawal, M. Lenormand and B. M. Matute. *Org. Lett*. 2012, **14**, 1456–1459.
19. Y-H. Chang, Y. Nakajima and F. Ozawa, *Organometallics*. 2013, **32**, 2210–2215.

20. (a) R. Ramachandran, G. Prakash, S. Selvamurugan, P. Viswanathamurthi, J. G. Malecki and V. Ramkumar. *Dalton Trans.,* 2014, **43**, 7889–7902; (b) R. Ramachandran and P. Viswanathamurthi, *Spectrochim. Acta, Part A* 2014, **103,** 53–61; (c) G. Prakash, R. Ramachandran, M. Nirmala, P. Viswanathamurthi and W. Linert, *Monatsh chem.* DOI: 10.1007/s00706-014-1300-z; (d) G. Prakash and P. Viswanathamurthi, *Spectrochim. Acta, Part A* 2014, **129**, 352–358.

21. For selected examples, see: (a) D. Palanimuthu, S. V. Shinde, K. Somasundaran and A. G. Samuelson, *J. Med. Chem*., 2013, **56**, 722–734; (b) J. L. Hickey and P. S. Donnelly, *Coord. Chem. Rev*., 2012, **256**, 2367–2380; (c) T. S. Lobana, R. Sharma, G. Bawa, S. Khanna, *Coord. Chem. Rev*., 2009, **253**, 977–1055; (d) P. V. Bernhardt, P. C. Sharpe, M. Islam, D. B. Lovejoy, D. S. Kalinowski, and D. R. Richardson, *J. Med. Chem.,* 2009**, 52,** 407–415; (e) A. G. Quiroga and C. N. Ranninger, *Coord. Chem. Rev*., 2004, **248**, 119–133; (f) J. S. Casas, M. S. G. Tasende and J. Sordo, *Coord. Chem. Rev*., 2000, **209**, 197−261; (g) S. Padhi and G. B. Kauffman, *Coord. Chem. Rev*., 1985, **63**, 127–160; (g) M. J. M. Campbell, *Coord. Chem. Rev*., 1975, **15**, 297−319.

22. For selected examples, see: (a) P. K. Suganthy, R. N. Prabhu and V. S. Sreedevi, *Tetrahedron Lett*., 2013, **54**, 5695–5698; (b) P. R. Verma, S. Mandal, P. Gupta and B. Mukhopadhyay, *Tetrahedron Lett*., 2013, **54**, 4914–4917; (c) R. N. Prabhu and R. Ramesh, *Tetrahedron Lett*., 2012, **53**, 5961–5965; (d) S. Datta, D. K. Seth, S. Gangopadhyay, P. Karmakar and S. Bhattacharya, *Inorg. Chim. Acta*, 2012, **392**, 118–130; (e) P. Paul, S. Datta, S. Halder, R. Acharyya, F. Basuli, R. J. Butcher, S.-M. Peng, G.-H. Lee, A. Castineiras, M. G. B. Drew and S. Bhattacharya, *J. Mol. Catal. A: Chem*., 2011, **344**, 62–73.

23. (a) G. Xie, P. Chellan, J. Mao, K. Chibale, and G. S. Smith , *Adv. Synth. Catal*. 2010, **352**, 1641– 1647

24. (a) J. Dutta and S. Bhattacharya, *RSC Adv*, 2013, **3**, 10707−10721; (b) J. Dutta, S. Datta, D. Kumar Seth and S. Bhattacharya, *RSC Adv*, 2012, **2**, 11751−11763 (c) P. Pelagatti, A. Venturini, A. Leporati, M. Carcelli, M. Costa, A. Bacchi, G. Pelizzi and C. Pelizzi, *J. Chem. Soc., Dalton Trans.,* 1998, 2715–2721.

25. U. Abram, K. Ortner, R. Gust and K. Sommer, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 735–744.

26. (a) A. Castineiras and R. Pedrido, *Dalton Trans.*, 2012, **41**, 1363−1372; (b) A. Castineiras and R. Pedrido, *Inorg. Chem.*, 2008, **47**, 5534–5536. (c)G. Argay, A. Kalman , L. Parkanyi , V. M. Leovac , I. D. Brceski and P. N. Radivojsa, *J. Coord. Chem.*, 2000, **51**, 9–19.

27. A. Castineiras, R. Pedrido and G. Perez-Alonso, *Eur. J. Inorg. Chem.*, 2008, 5106–5111.

28. A. Castineiras and R. Pedrido, *Dalton Trans.*, 2010, **39**, 3572–3584.

29. A. Castineiras and R. Pedrido, *Inorg. Chem.,* 2009, **48***,* 4847–4855.

30. (a) P. Anitha, P. Viswanathamurthi, D. Kesavan and R. J. Butcher *J. Coord. Chem.* DOI: 10.1080/00958972.2014.977269; (b) M. Nirmala, R. Manikandan, G. Prakash and P. Viswanathamurthi, *Appl. Organometal. Chem,.* 2014, **28**, 18–26; (c) P. Anitha, R. Manikandan, A. Endo, T. Hashimoto and P. Viswanathamurthi, *Spectrochim. Acta, Part A* 2012, **99**, 174−180.
31. J. E. Hoots, T. B. Rauchfuss and D. A. Wrobleski*, Inorg. Synth.* 1982**, 21**, 175−178.
32. F. Basuli, S. M. Peng and S. Bhattacharya, *Inorg. Chem.*, 2001, **40**, 1126–1133.
33. (a) T. F. Vaughan, D. J. Koedyk and J. L. Spencer, *Organometallics*, 2011, **30**, 5170–5180; (b) O. Del Campo, A. Carbayo, J. V. Cuevas, G. Garcia-Herbosa and A. Munoz, *Eur. J. Inorg. Chem.,* 2009, 2254–2260; (c) K. S. Coleman, M. L. H. Green, S. I. Pascu, N. H. Rees, A. R. Cowley and L. H. Rees, *J. Chem. Soc., Dalton Trans.,* 2001, 3384–3395.
34. (a) T. S. Lobana, G. Bawa, A. Castineiras, R. J. Butcher, B. J. Liaw and C. W. Liu, *Polyhedron* 2006, **25**, 2897–2903; (b) F. Basuli, S. M. Peng and S. Bhattacharya, *Inorg. Chem.* 2000, **39**, 1120–1127; (c) I. Pal, F. Basuli, T. C. W. Mak and S. Bhattacharya, *Angew. Chem. Int. Ed.* 2001, **40**, 2923–2925; (d) S. Dutta, F. Basuli, S. M. Peng, G. H. Lee and S. Bhattacharya, *New J. Chem.* 2002, **26**, 1607–1612; (e) F. Basuli, S. M. Peng and S. Bhattacharya, *Inorg. Chem.* 1997, **36**, 5645–5647.
35. (a) L. D. Brown, S. D. Robinson, A. Sahajpal and J. A. Ibers, *Inorg. Chem.* 1977, **16**, 2728–2735. (b) M. I. Bruce, J. Howard, I. W. Nowell, G. Shaw and P. Woodward, *J.*

Chem. Soc., Chem. Commun. 1972, 1041–1042; (c) A. C. Skapski and P. G. H. Troughton, *Chem. Commun. (London)* **1968**, 1230–1231.

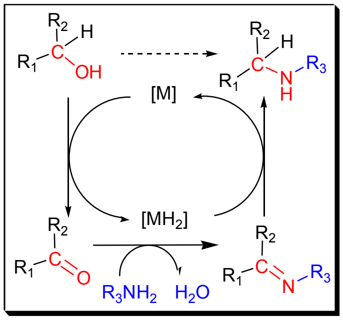
36. P. Kalaivani, R. Prabhakaran, E. Vaishnavi,b T. Rueffer, H. Lang, P. Poornima, R. Renganathan, V. Vijaya Padmad and K. Natarajan, *Inorg. Chem. Front.*, 2014, **1**, 311-324
37. R. Prabhakaran, P. Kalaivani, R. Huang, M. Sieger, W. Kaim, P. Viswanathamurthi, F. Dallemer and K. Natarajan, *Inorg. Chim. Acta,* 2011, **376**, 317–324.
38. V. Mahalingam, N. Chitrapriya, F. R. Fronczek and K. Natarajan, *Polyhedron*, 2008, **27** 1917–1924
39. A. Castineiras and R. Pedrido, *Dalton Trans.,* 2012, **41**, 1363–1372.
40. V. Mahalingam, N. Chitrapriya, F. R. Fronczek and K. Natarajan, *Polyhedron,* 2010, **29**, 3363–3371.
41. S. Dutta, F. Basuli, A. Castineiras, S-M. Peng, G-H. Lee, and S. Bhattacharya, *Eur. J. Inorg. Chem.* 2008, 4538–4546
42. P. Kalaivani, R. Prabhakaran, P. Poornima, F. Dallemer, K. Vijayalakshmi, V. Vijaya Padma, and K. Natarajan, *Organometallics,* 2012, **31**, 8323−8332.
43. P. Crochet, J. Gimeno, S. Garcıa-Granda and J. Borge, *Organometallics,* 2001, **20**, 4369−4377.

44. C.-C. Lee, W.-Y. Chu, Y.-H. Liu, S.-M. Peng and S.-T. Liu, *Eur. J. Inorg. Chem.,* 2011, 4801–4806
45. (a) A. J. A. Watson and J. M. J. Williams, *Science*, 2010, **329**, 635−636; (b) K. I. Fujita, Y. Enoki and R. Yamaguchi, *Tetrahedron*, 2008, **64**, 1943−1954; (c) R. Yamaguchi, S. Kawagoe, C. Asai and K. I. Fujita, *Org. Lett*., 2008, **10**, 181−184; (d) G. Cami-Kobeci and J. M. J. Williams, *Chem. Commun.*, 2004, 1072−1073; (e) D. Hollmann, A. Tillack, D. Michalik, R. Jackstell and M. Beller, *Chem. Asian J.*, 2007, **2**, 403−410; (f) A. Tillack, D. Hollmann, D. Michalik and M. Beller, *Tetrahedron Lett.*, 2006, **47**, 8881−8885.

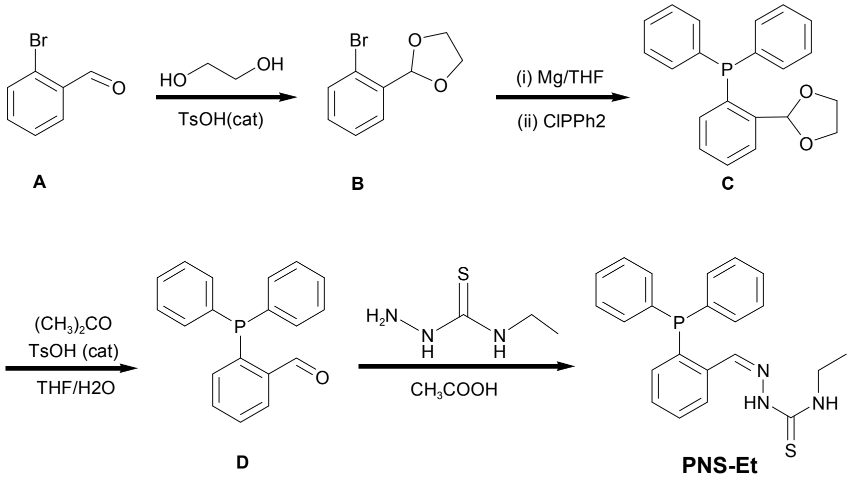
46. (a) D. C. Cole, W. J. Lennox, S. Lombardi, J. W. Ellingboe, R. C. Bernotas, G. J. Tawa, H. Mazandarani, D. L. Smith, G. Zhang, J. Coupet and L. E. Schechter, *J. Med. Chem.* 2005, **48**, 353–356; (b) M. Banerjee, A. Poddar, G. Mitra, A. Surolia, T. Owa and B. Bhattacharyya, *J. Med. Chem.* 2005, **48**, 547–555; (c) A. Kleemann, J. Engel, B.

Kutscher and D. Reichert, *Eds. Pharmaceutical Substances, Syntheses, Patents, Applications*; Thieme: Stuttgart, 1999; (d) A. Natarajan, Y. Guo, F. Harbinski, Y-H. Fan, H. Chen, L. Luus, J. Diercks, H. Aktas, M. Chorev and J. A. Halperin, *J. Med. Chem.* 2004, **47**, 4979–4982; (e) N. K. U. Koehler, et al. *J. Med. Chem.* 2004, **47**, 4989–4997.

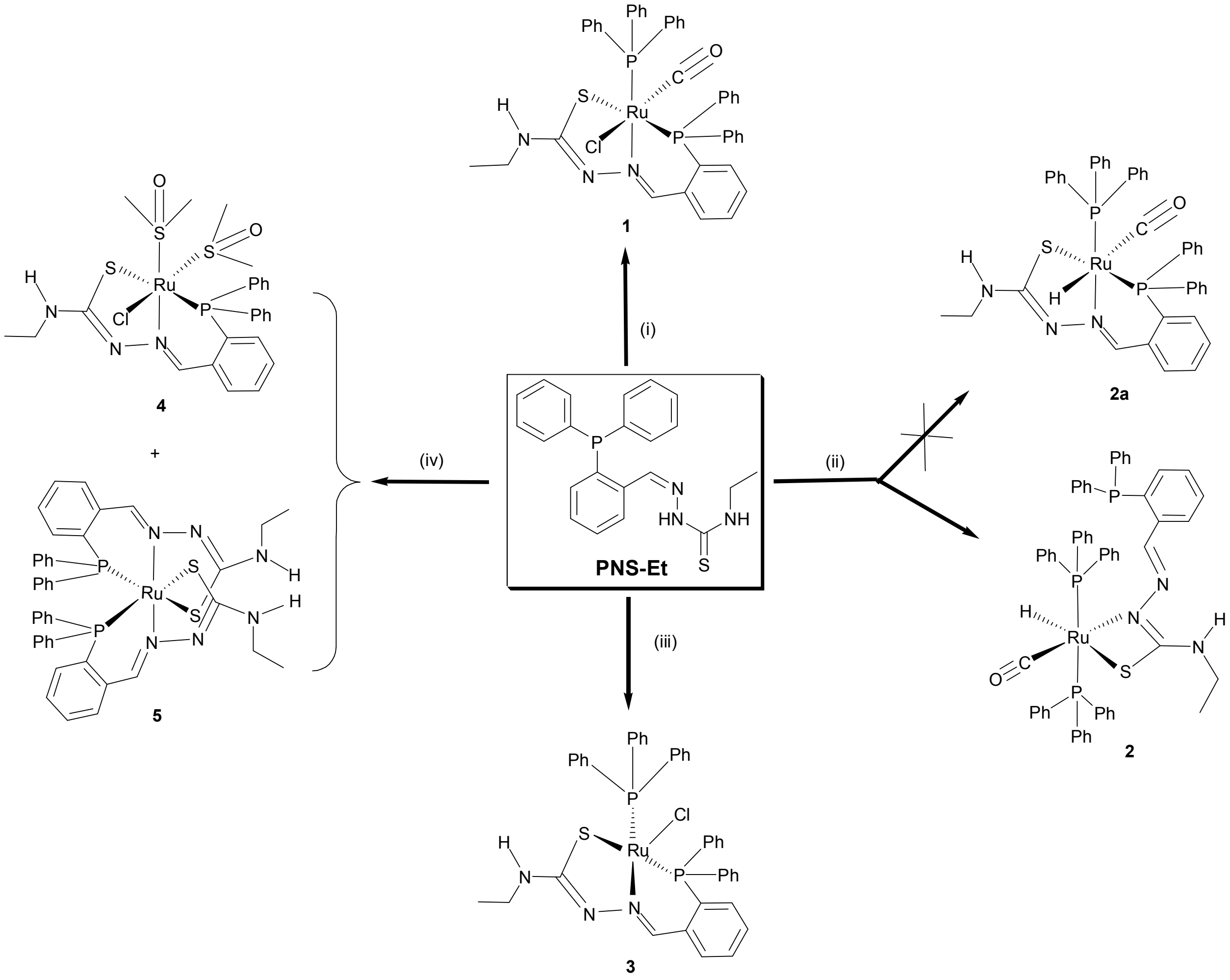
47. (a) L. F. Fieser, M. Fieser, *Reagents for Organic Synthesis*; Wiley: New York, 1967, **1**, 1179. (b) R. Cremlyn, *Organosulfur Chemistry: An Introduction*; John Wiley and Sons: New York, 1996.
48. (a) A. Shaabani, E. Soleimani and A. H. Rezayan, *Tetrahedron Lett.* 2007, **48**, 2185–2188; (b) W. Deng, L. Liu, C. Zhang, M. Liu and Q.-X. Guo, *Tetrahedron Lett.* 2005, **46**, 7295–7298; (c) G. Burton, P. Cao, G. Li and R. Rivero, *Org. Lett.* 2003, **5**, 4373–4376.
49. S. Caddick, J. D. Wilden and D. B. Judd, *J. Am. Chem. Soc.* 2004, **126**, 1024–1025.
50. M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson and J. M. J. Williams, *J. Am. Chem. Soc.* 2009, **131**, 1766–1774.
51. F. Shi, M. K. Tse, S. L Zhou, M. M. Pohl, J. Radnik, S. Huebner, K. Jaehnisch, A. Bruecker and M. Beller, *J. Am. Chem. Soc.* 2009, **131**, 1775–1779.
52. F. Shi, M. K. Tse, X. Cui, D. Gordes, D. Michalik, K. Thurow, Y. Deng and M. Beller. *Angew. Chem. Int. Ed*. 2009, **48**, 5912–5915.
53. (a) Y-H. Chang, Y. Nakajima and F. Ozawa, *Organometallics*, 2013, **32**, 2210–2215; (b) F. E. Fernandez, M. Carmen Puerta and P. Valerga, *Organometallics*, 2012, **31**, 6868–6879; (c) C. Xu, L. Y. Goh and S. A. Pullarkat, *Organometallics,* 2011, **30**, 6499−6502; (d) S. Kegnæs, J. Mielby, U. V. Mentzel, C. Christensen and A. Riisager, *Green Chem*., 2010, **12**, 1437−1441.
54. N. Ahmed, S. J. Levison, S. D. Robinson and M. F. Uttley, *Inorg. Synth*., 1974, **15**, 48−52.
55. P. C. Junk and J. W. Steed, *J. Organomet. Chem*. 1999, **587**, 191–194.
56. S. K. Sharma, V. K. Srivastava and R. V. Jasra, *J. Mol. Catal. A: Chem*. 2006, **245**, 200−209.
57. I.P. Evans, A. Spencer and J. Wilkinson, *J. Chem. Soc., Dalton Trans*. 1973, **2**, 204−209.
58. G. M. Sheldrick, *Acta Crystallogr*. 2008, **A64**, 112−122.



Scheme 1 Borrowing hydrogen strategy for C-N bond formation reaction

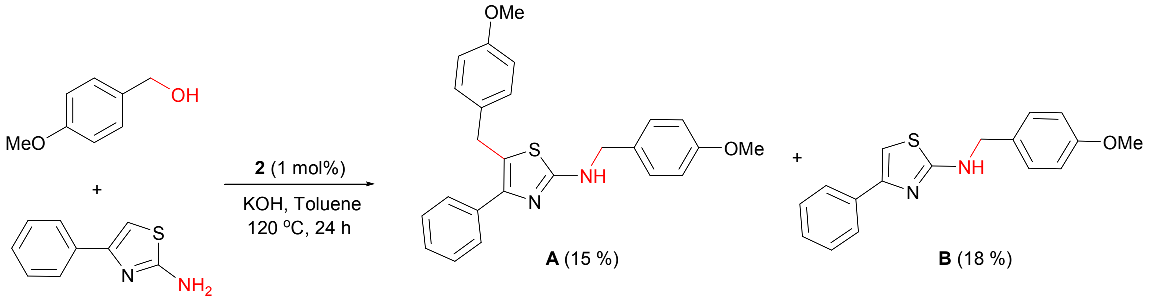


Scheme 2 Synthesis of ligand (PNS-Et)

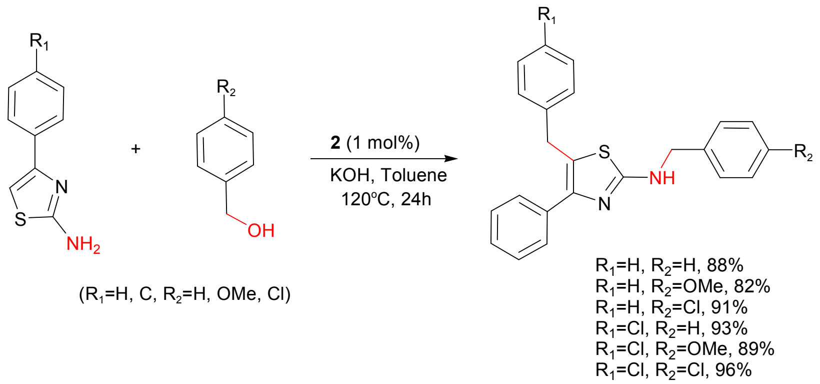


Scheme 3 Synthesis of ruthenium(II) complexes (**1-5**). (i) [RuHCl(CO)(PPh$_3$)$_3$], C$_2$H$_5$OH, reflux 8h (ii) [RuH$_2$(CO)(PPh$_3$)$_3$], C$_2$H$_5$OH /CH$_2$Cl$_2$, reflux 12h (iii) [RuCl$_2$(PPh$_3$)$_3$], C$_2$H$_5$OH /CH$_2$Cl$_2$, reflux 8h (iv) Cis-[RuCl$_2$(Me$_2$SO)$_4$], C$_2$H$_5$OH, reflux 12h.

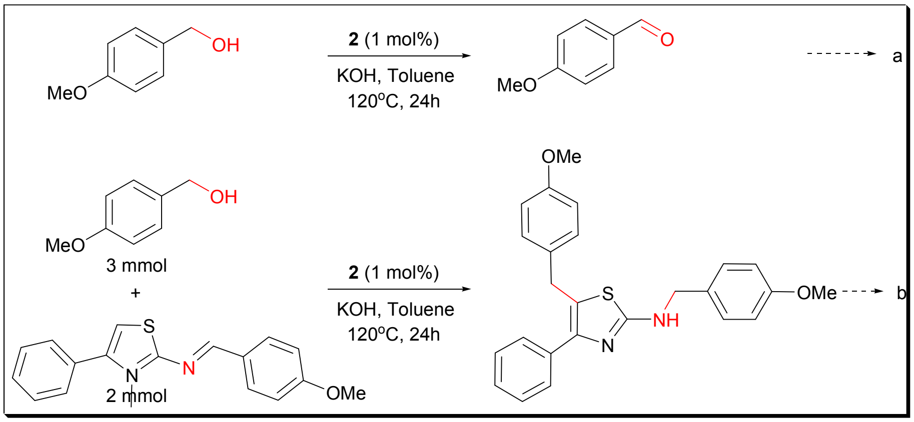
.



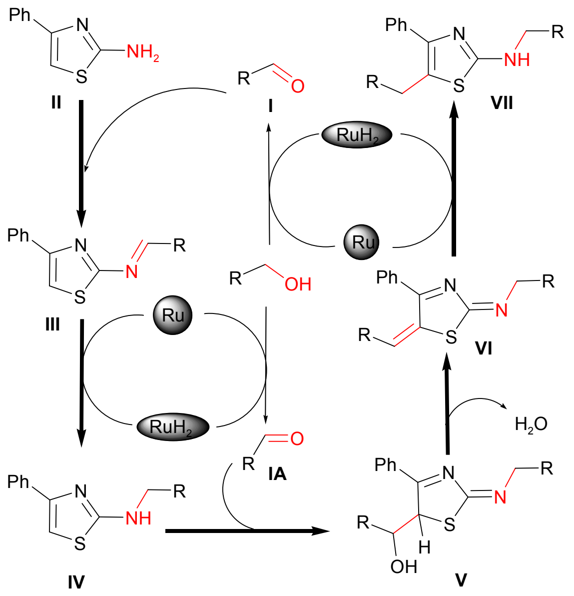
Scheme 4 Alkylation of 4-phenylthiazol-2-amine with various alcohols



Scheme 5 N_1, C_5-Dialkylation of 4-phenylthiazol-2-amine with various alcohols



Scheme 6 Controlled experiments for elucidation of mechanism



Scheme 7 Plausible mechanism for *N*$_1$, *C*$_5$-dialkylation

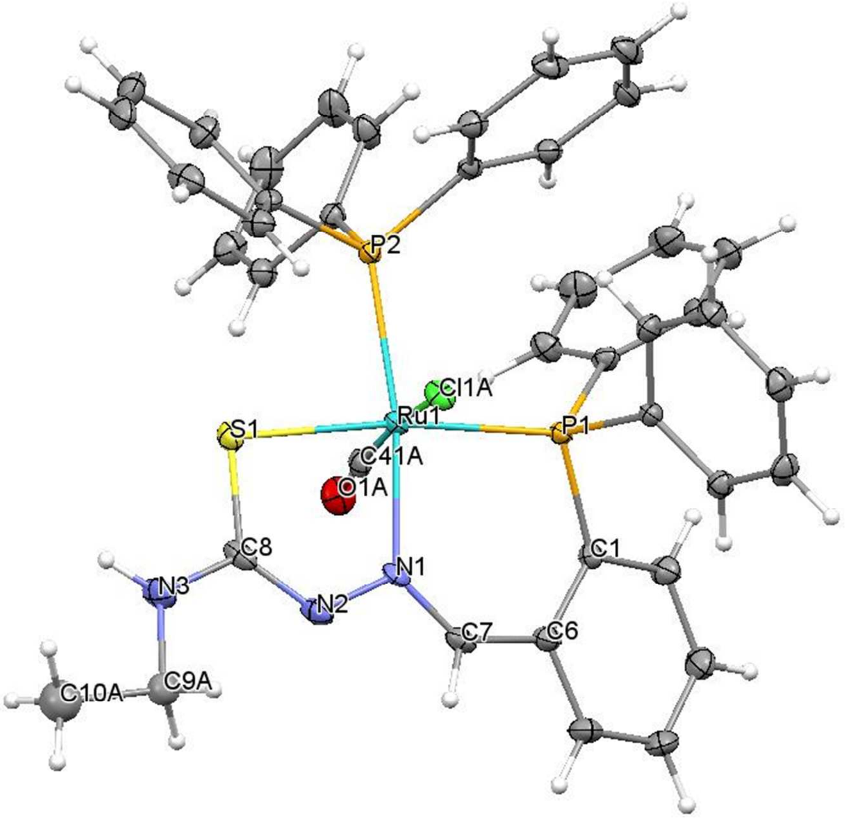


Figure 1 Molecular structure of **1**. Ellipsoids are shown at the 35% probability level. The disordered terminal ethyl group, chloride and carbonyl ligand of the structure have been omitted for clarity. Selected bond distances (Å) and bond angles (deg): Ru(1)–C(41A) = 1.855(9), Ru(1)−N(1) = 2.141(3), Ru(1)−P(1) = 2.3382(8), Ru(1)−S(1) = 2.3831(8), Ru(1)− P(2) = 2.3890(8), Ru(1)−Cl(1A) = 2.424(2); C(41A)−Ru(1)−N(1) = 86.3(3), C(41A)−Ru(1)−P(1) = 89.7(3), N(1)−Ru(1)−P(1) = 90.69(7) = C(41A)−Ru(1)−S(1) = 89.0(3), N(1)−Ru(1)−S(1) = 81.48(7), P(1)−Ru(1)−S(1) = 172.13(3), C(41A)−Ru(1)−P(2) = 96.4(3), N(1)−Ru(1)−P(2) = 169.60(7), P(1)−Ru(1)−P(2) = 99.33(3), S(1)−Ru(1)−P(2) = 88.53(3), C(41A)−Ru(1)−Cl(1A) = 171.5(3), N(1)−Ru(1)−Cl(1A) = 85.32(9).

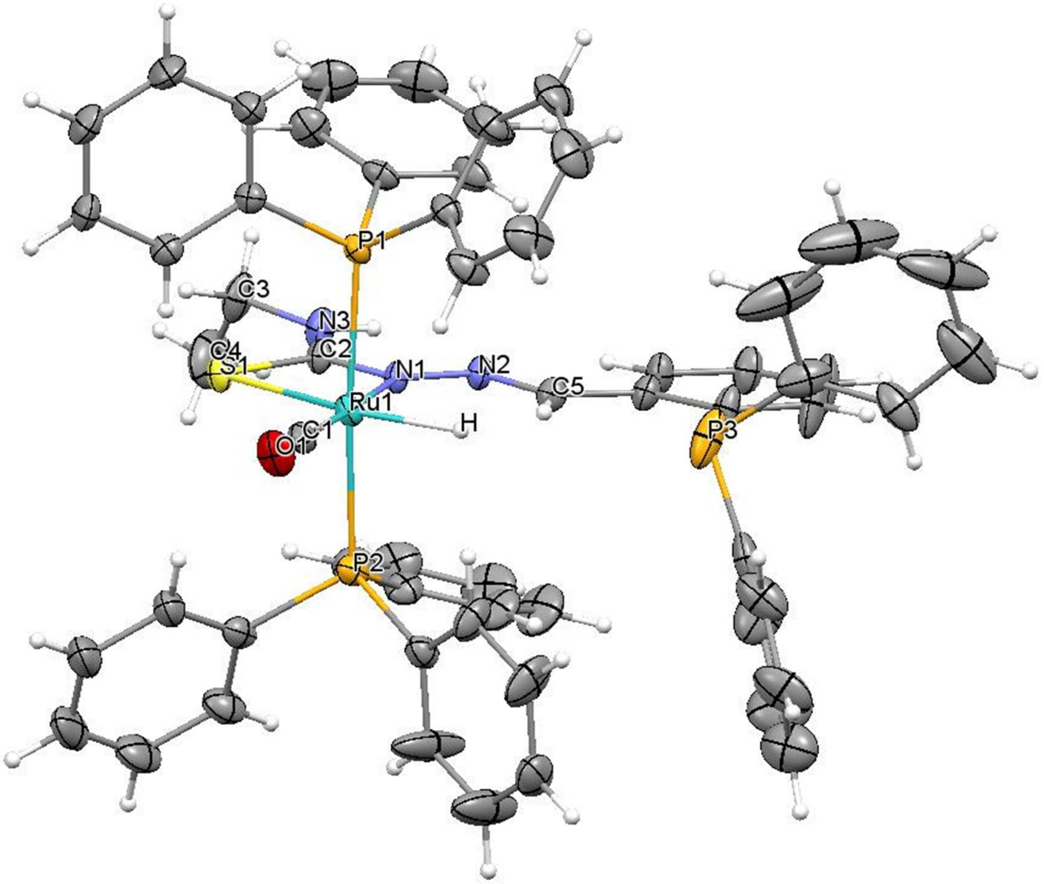


Figure 2 Molecular structure of **2**. Ellipsoids are shown at the 35% probability level. The disordered phenyl group in triphenylphosphine has been omitted for clarity. Selected bond distances (Å) and bond angles (deg): Ru(1)−H(1) = 1.88(4), Ru(1)−S(1) = 2.5568(10), Ru(1)−P(1) = 2.3665(10), Ru(1)−P(2) = 2.3546(11), Ru(1)−N(1) = 2.128(3), Ru(1)−C(1) = 1.839(4), S(1)−Ru(1)−H = 165.7(13), P(1)−Ru(1)−H 90.1(12), P(1)−Ru(1)−S(1) = 88.92(4), P(2)−Ru(1)−H = 87.6(12), P(2)−Ru(1)−S(1) = 92.42(4), P(2)−Ru(1)−P(1) = 175.60(4), N(1)−Ru(1)−H = 101.4(13), N(1)−Ru(1)−S(1) = 64.32(8), N(1)−Ru(1)−P(1) = 88.64(8), N(1)−Ru(1)−P(2) = 88.17(8), C(1)−Ru(1)−H = 81.6(13), C(1)−Ru(1)−S(1) = 112.66(12), C(1)−Ru(1)−P(1) = 91.14(12), C(1)−Ru(1)−P(2) = 92.21(12), C(1)−Ru(1)−N(1) = 176.98(15).

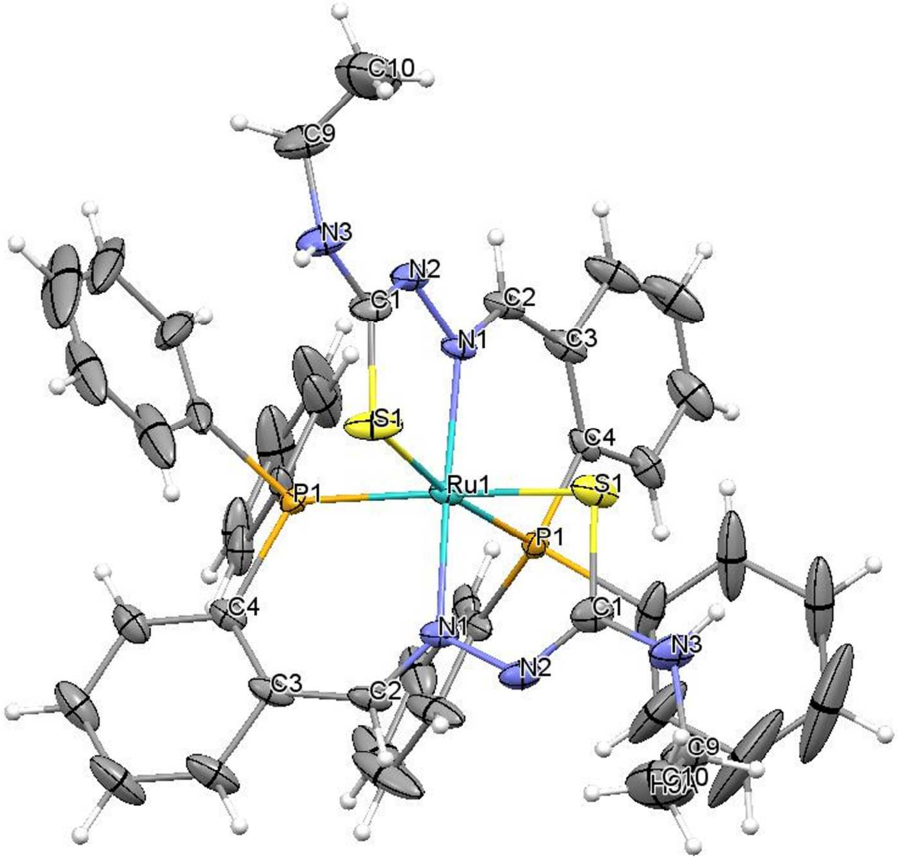


Figure 3 Molecular structure of **5**. Ellipsoids are shown at the 35% probability level. Selected bond distances (Å) and bond angles (deg): Ru(1)−S(1) = 2.3854(12), Ru(1)−S(1) = 2.3854(12), Ru(1)−P(1) = 2.3048(10), Ru(1)−P(1) = 2.3047(10), Ru(1)−N(1) = 2.062(3), Ru(1)−N(1) = 2.062(3); S(1)−Ru(1)−S(1) = 85.11(8), P(1)−Ru(1)−S(1) = 88.66(5), P(1)−Ru(1)−S(1) = 88.66(5), P(1)−Ru(1)−S(1) = 172.06(5), P(1)−Ru(1)−S(1) = 172.06(5), P(1)−Ru(1)−P(1) = 97.95(5), N(1)−Ru(1)−S(1) = 82.10(9), N(1)−Ru(1)−S(1) = 93.02(9) = N(1)−Ru(1)−S(1) = 93.01(9), N(1)−Ru(1)−S(1) = 82.10(9), N(1)−Ru(1)−P(1) = 93.34(9), N(1)−Ru(1)−P(1) = 91.00(9), N(1)−Ru(1)−P(1) = 93.34(9), N(1)−Ru(1)−P(1) = 91.00(9), N(1)−Ru(1)−N(1) = 173.40(17).

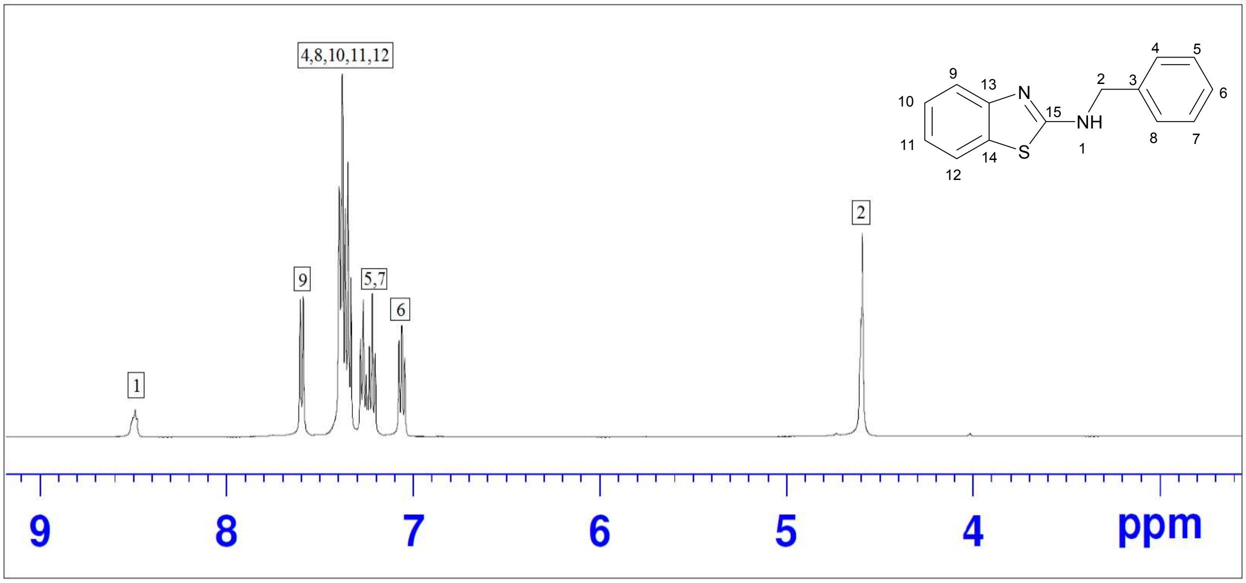


Figure 4 ^{1}H NMR spectrum of *N*-Benzylbenzo[d]thiazol-2-amine

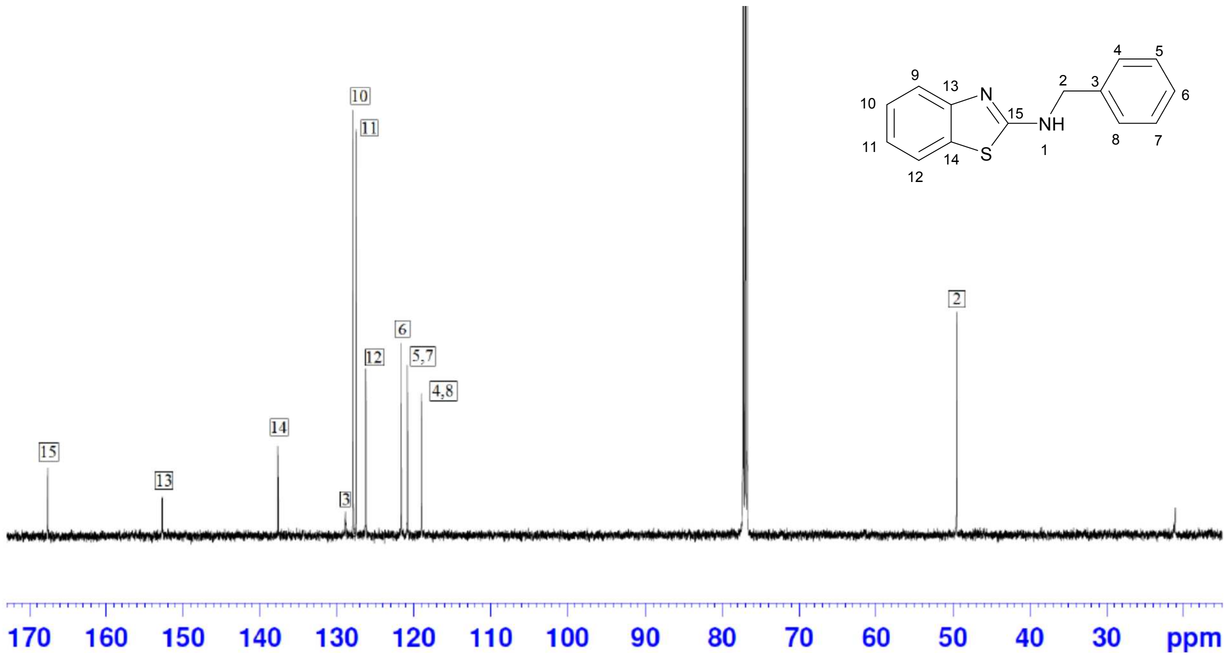


Figure 5 ^{13}C NMR spectrum of *N*-Benzylbenzo[d]thiazol-2-amine

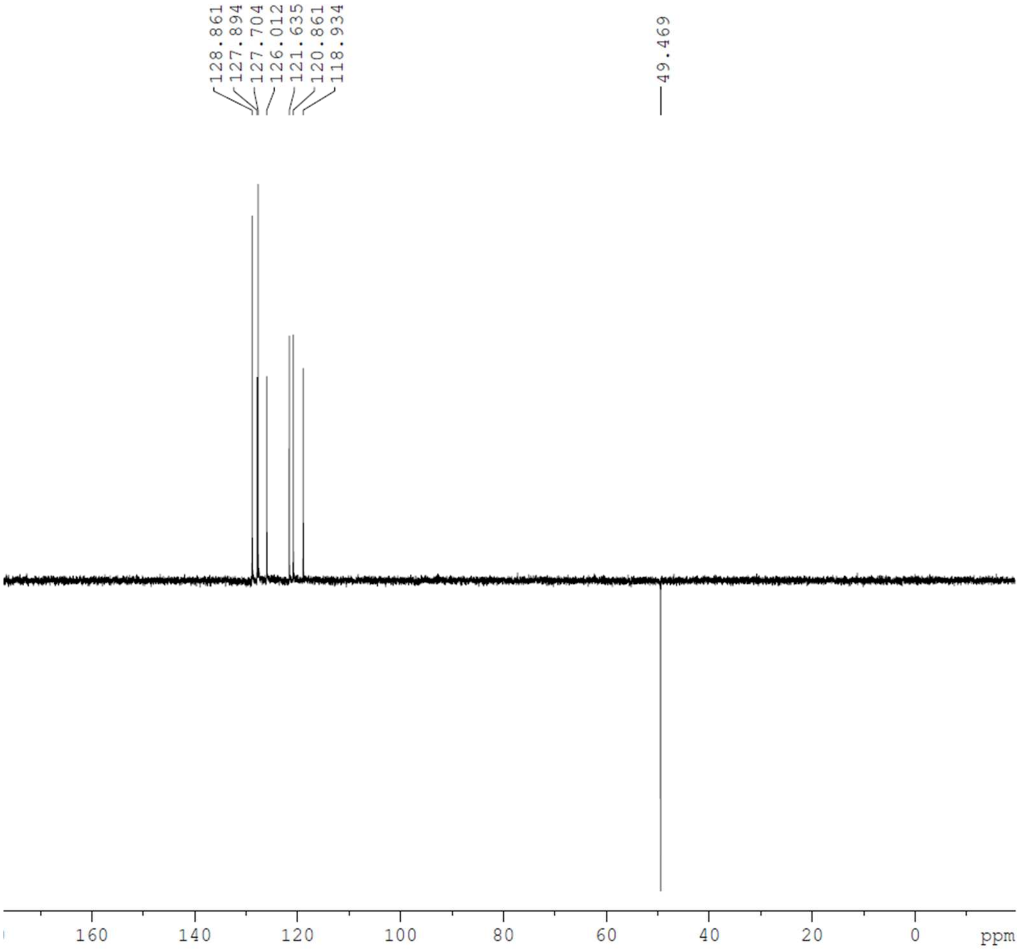


Figure 6 DEPT spectrum of *N*-Benzylbenzo[d]thiazol-2-amine

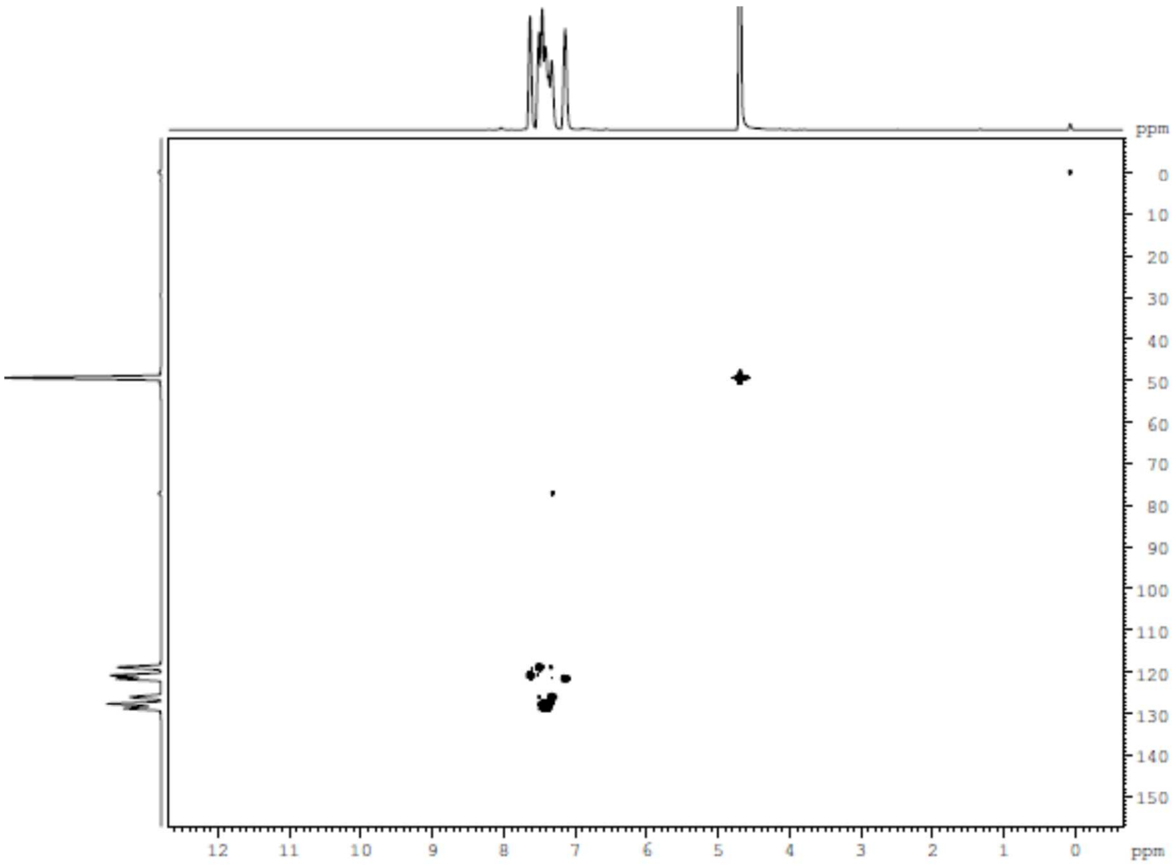
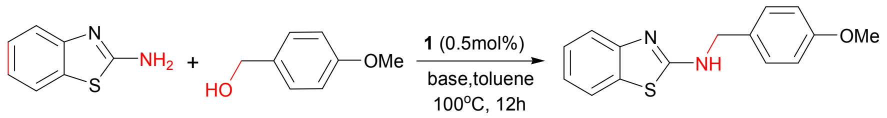


Figure 4 HSQC spectrum of *N*-Benzylbenzo[d]thiazol-2-amine

Table 1 Experimental data for crystallographic analyses

	complex 1	**complex 2**	**complex 5**
chem formula	$C_{41}H_{36}ClN_3OP_2RuS$	$C_{59}H_{52}N_3OP_3RuS$	$C_{44}H_{42}N_6P_2RuS_2$
formula wt	817.25	1045.07	881.97
cryst syst	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P\bar{1}$	$C222_1$
cryst color and shape	orange/polyhedra	green/prism	dark red/polyhedra
cryst size (mm)	0.50 x 0.26 x 0.18	0.29 x 0.09 x 0.05	0.34 x 0.28 x 0.16
a (Å)	14.3401(5)	9.4861(4)	11.080(2)
b (Å)	16.5933(5)	13.3046(5)	22.178(4)
c (Å)	15.1214(5)	21.9391(9)	16.849(3)
α (deg)	90	86.469 (3)	90
β (deg)	96.3390(10)	79.675(3)	90
γ (deg)	90	71.36 (3)	90
V (Å^3)	3576.1(2)	2581.15(18)	4140.2(14)
Z	4	2	4
T (K)	296(2)	295(2)	295(2)
D$_c$ (g cm^{-3})	1.518	1.345	1.412
μ (mm^{-1})	0.700	0.481	0.596
F(000)	1672	1080	1816
scan range (deg)	$1.43 < 2\theta > 28.55$	$3.76 < 2\theta > 25.05$	$3.04 < 2\theta > 25.05$
index ranges	-19< = h< = 19 -21< = k< = 22 -20< = l< = 18	-11< = h< = 11 -15< = k< = 15 -26< = l< = 26	-12< = h< = 13 -26< = k< = 20 -16< = l< = 20
no. of unique rflns	38482	23377	24015
no. of rflns used [$I > 2\sigma(I)$]	8983	9123	3654
R$_{int}$	0.392	0.0481	0.0328
data/restraints/parameters	8983/0/480	9123/0/637	3654/0/238
goodness of fit	0.864	1.017	1.096
final R$_1$ and wR$_2$ indices [$I > 2\sigma(I)$]	0.0392, 0.1076	0.0481, 0.1094	0.0328, 0.0789
R$_1$and wR$_2$ indices (all data)	0.0694, 0.1076	0.0758, 0.1094	0.0343, 0.0789

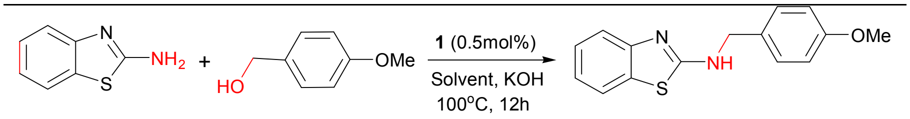
Table 2 Screening of bases for *N*-alkylation of 2-aminobenzothiazole with 4-methoxybenzyl alcohol[a]



Entry	Base	Amount of base (mol%)	Yield (%)[c]
1	Na_2CO_3	50	-
2	K_2CO_3	50	15
3	Cs_2CO_3	50	>2
4	KOH	25	87
5[b]	KOH	50	-
6	KOH	50	96
7	KOH	100	95
8	NaOH	50	69
9	NaO(*t*-Bu)	25	44
10	NaO(*t*-Bu)	50	56
11	KO(*t*-Bu)	100	64

[a] Reaction conditions: 2.00 mmol of 2-aminobenzothiazole, 2.00 mmol of 4-methoxybenzyl alcohol, base (25-100 mol%) and catalyst (0.5 mol %) in 2 mL of toluene at 100 °C. [b] Room temperature. [c] Yields were calculated after isolation of the pure *N*-(4-methoxybenzyl)benzothiazol-2-amine through short column chromatography using silica gel (100–200 mesh).

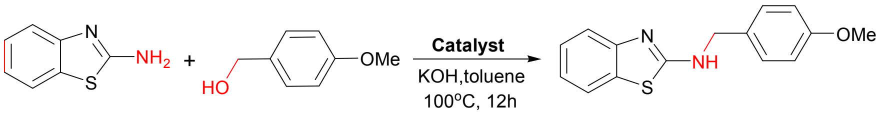
Table 3 Screening of solvent for *N*-alkylation of 2-aminobenzothiazole with 4-methoxybenzyl alcohol[a]



Entry	Sovent	Yield (%)[b]
1	1,4-dioxane	7
2	DMF	15
3	*o*-xylene	63
4	Toluene	96
5	H_2O	-
6	Benzene	22
7	THF	-
8	Ethanol	20

[a]Reaction conditions: 2.00 mmol of 2-aminobenzothiazole, 2.00 mmol of 4-methoxybenzyl alcohol, KOH (50 mol%) and catalyst (0.50 mol %) in 2 mL of solvent at 100 °C. [b]Yields were calculated after isolation of the pure *N*-(4-methoxybenzyl)benzothiazol-2-amine through short column chromatography using silica gel (100–200 mesh).

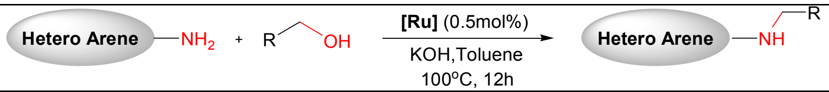
Table 4 Catalyst screening for *N*-alkylation of 2-aminobenzothiazole with 4-methoxybenzyl alcohol[a]

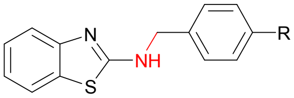
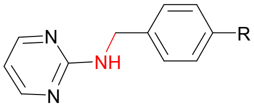
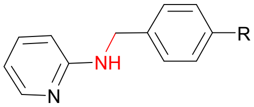
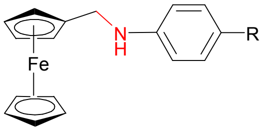
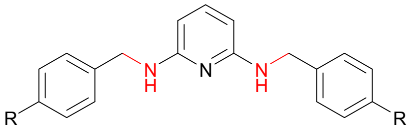


Entry	Catalyst	Amount of catalyst (mol%)	TON[b]	Yield (%)[c]
1	**1**	0.15/0.25/0.5	560/348/192	78/87/96
2	**2**	0.15/0.25/0.5	560/364/196	84/91/98
3	**3**	0.15/0.25/0.5	480/340/182	72/85/91
4	**4**	0.15/0.25/0.5	373/236/122	56/59/61
5	**5**	0.15/0.25/0.5	287/204/116	43/51/58

[a] Reaction conditions: 1.00 mmol of 2-aminobenzothiazole, 1.00 mmol of 4-methoxybenzyl alcohol, KOH (50 mol%) and catalyst (0.15-0.50 mol %) in 2 mL of toluene at 100 °C. [b] Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t. [c] Yields were calculated after isolation of the pure *N*-(4-methoxybenzyl)benzothiazol-2-amine through short column chromatography using silica gel (100–200 mesh).

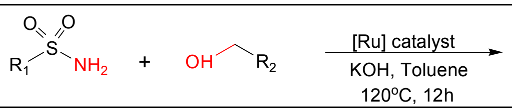
Table 5 N-Alkylation of various heteroaromatic amines with alcohols[a]

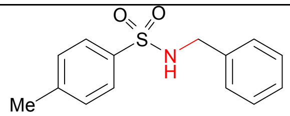
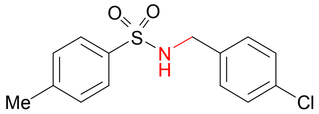
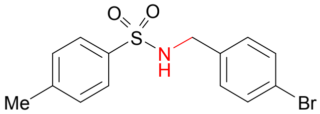
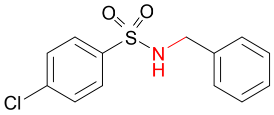
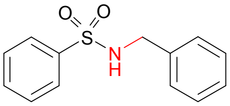
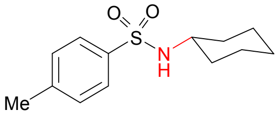
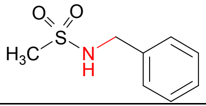


Entry	Product	R	Yield(%)[c]		
			Catalyst **1**	Catalyst **2**	Catalyst **3**
1		OMe	96	98	91
2		−H	84	97	81
3		−Me	86	94	76
4		−Cl	96	99	93
5		−Br	91	95	89
6		−H	86	93	91
7		−Me	84	90	86
8		−OMe	88	92	85
9		−Cl	90	97	87
10		−Br	89	94	91
11		−H	83	93	86
12		−Me	79	83	74
13		−OMe	85	89	78
14		−Cl	92	96	90
15		−Br	89	96	87
16		−H	67	79	59
17		−OMe	76	84	76
18		−Cl	83	91	74
19		−Br	81	87	76
20[b]		−Me	74	90	70
21[b]		−Cl	86	94	73
22[b]		−Br	81	92	74

[a] Reaction conditions: 2.00 mmol of heterocyclic amines, 2.00 mmol of alcohol, KOH (50 mol%), catalyst (0.5 mol %) in 2 mL of toluene at 100 °C. [b] 4.00 mmol of alcohols were used. [c] Yields were calculated after isolation of the pure *N*-alkylated amine through short column chromatography using silica gel (100−200 mesh).

Table 6 *N*-Alkylation of sulfonamides[a]



Entry	Product	Yield (%)[b]		
		1	**2**	**3**
1		82	91	84
2		95	99	85
3		86	94	82
4		93	97	89
5		88	92	87
6		62	74	71
7		21	54	46

[a] Reaction conditions: 2.00 mmol of sufonamides, 2.00 mmol of alcohol, KOH (50 mol%), catalyst (0.5 mol %) in 2 mL of toluene at 120 °C. [b] Yields were calculated after isolation of the pure *N*-alkylated amine through short column chromatography using silica gel (100–200 mesh).

Graphical Abstract

We report the coordination flexibility of phosphino-thiosemicarbazone in ruthenium(II) complexes, together with their catalytic properties with regards to *N*-alkylation, *N,N'*-dialkylation and N_1,C_5-dialkylation of amines using KOH as the base.