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Ruthenium Complexes Bearing α-Diimine Ligands and Their Catalytic Applications in N-Alkylation of Amines, α-Alkylation of Ketones, and β-Alkylation of Secondary Alcohols

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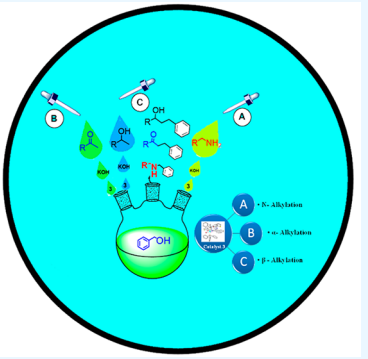
ABSTRACT: New Ru(II) complexes encompassing α-diimine ligands were synthesized by reacting ruthenium precursors with α-diimine hydrazones. The new ligands and Ru(II) complexes were analyzed by analytical and various spectroscopic methods. The molecular structures of $\mathbf{L_1}$ and complexes **1**, **3**, and **4** were determined by single-crystal XRD studies. The results reveal a distorted octahedral geometry around the Ru(II) ion for all complexes. Moreover, the new ruthenium complexes show efficient catalytic activity toward the C−N and C−C coupling reaction involving alcohols. Particularly, complex **3** demonstrates effective conversion in N-alkylation of aromatic amines, α-alkylation of ketones, and β-alkylation of alcohols.



INTRODUCTION

The development of catalytic ways to form carbon−nitrogen and carbon−carbon bonds is vital in organic synthesis because they are fundamental in the creation of the complex structures observed in a huge variety of medicinal, agrochemical, surfactant, and bioactive molecules.[1] The reduction of imines, nitriles, and nitro compounds; reductive amination of carbonyl compounds;[2] hydroamination[3] or hydroaminomethylation[4] of unsaturated compounds; and metal-catalyzed amination of aryl halides[5] are just a few examples of the traditional ways to form the C−N bond, while nucleophilic replacement reactions, utilizing an organometallic reagent and an organic electrophile, were reported for C−C bond formation.[6] However, traditional processes frequently necessitate multistep procedures or environmentally unfriendly organic or organometallic coupling partners, as well as a large number of bases, generating a large amount of waste.[7] As a result, for future acceptable methods, more productive and green alkylation processes using nontoxic and readily available starting materials would be appealing. To be successful in this regard, any novel process should use inexpensive and widely available chemical starting materials and prevent the generation of considerable volumes of byproducts. Recently, nontoxic and readily available alcohols were utilized as alkylating agents in many reactions including a catalytic "hydrogen borrowing" system.[8] Because of its atom economy, the "hydrogen borrowing methodology" or "hydrogen auto transfer" has received a lot of interest.[9,10] These reactions release water as the only byproduct, making them green. Furthermore, rather than oil-based combinations, the employment of alcohols as substrate for C−N and C−C bond formation reactions is appealing because they are simple, are easy to maintain and store, and offer a limitless variety. For the successful alkylation involving alcohol in HBMS (hydrogen borrowing methodology strategy), both heterogeneous and homogeneous catalysts have been used. However, there has been a growing interest in homogeneous catalysts based on ruthenium metal complexes in recent years (Figure 1).[11,12]

In this interesting circumstance, Grigg et al.[13] and Watanabe et al.[14] presented a segment of the foremost homogeneous stimuli for N-alkylation reactions in 1981−1985, and based on that, more unique catalysts operating in mild conditions were developed. Shvo's ruthenium catalyst system,[15] described by Beller's group, and Williams and co-workers' ruthenium dimer catalyst[16] are two notable examples of ruthenium complexes that are known to catalyze alkylation. Matute and associates used Ru(*II*)CNN[17] pincer-type complexes as catalysts for C−N bond formation reaction by N-alkylated amines with excellent results. Crabtree et al.[18] employed air-stable pyrimidine-functionalized-NHC complexes of Ir and Ru as catalysts for both β-alkylation of secondary alcohols and N-alkylation of amines with primary alcohols. Bruneau and Valerga effectively applied Ru^{II} complexes containing chelating

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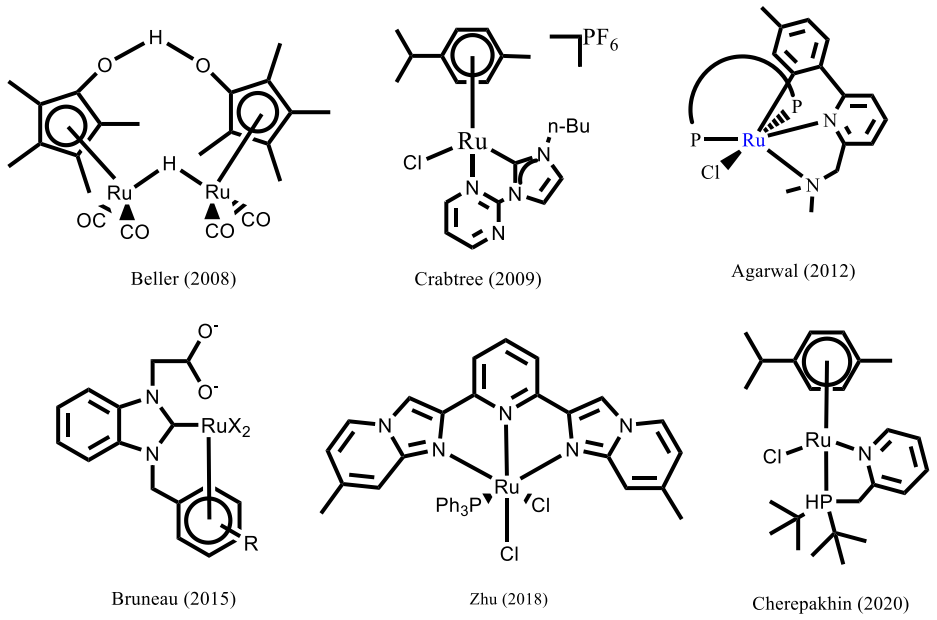

Figure 1. Reported catalysts for the formation of C−N and C−C bonds.

NHCs functionalized with different types of groups as efficient catalysts for N-alkylation of amines.[19] Cherepakhin and Williams used a ruthenium *p*-cymene complex [(η^6-cymene)-$RuCl(PyCH_2PtBu_2)$] as a precatalyst for the synthesis of secondary amines through a hydrogen borrowing mechanism, and it was successfully applied to several heterocyclic carbonyl substrates.[20]

On the other hand, due to its environmentally benign nature, direct alkylation of secondary alcohols catalyzed by a transition-metal catalyst has attracted wide attention in recent years. Many active transition metal catalysts have been reported for the above reaction. Cho et al. utilized a $RuCl_2(PPh_3)_3$ catalyst for direct β-alkylation. However, the catalyst was active only in the presence of a hydrogen acceptor and hydrogen donor.[21] Martínez's group reported $RuCl_2(DMSO)_4$ as an effective catalyst for β-alkylation reactions.[22] Ruthenium complexes containing a chelating N-heterocyclic carbene and other types of ligands were efficiently used for direct β-alkylation of secondary alcohols with primary alcohols.[23] Kundu et al. reported a ruthenium complex containing 6,6′-dihydroxy-2,2′-bipyridine as the most effective catalyst for β-alkylation of secondary alcohols with TOFs up to 797.6. As a dynamic push for β-alkylation of 2° alcohols with 1° alcohols, ruthenium hydride complexes containing unsymmetrical NNN ligands were used as catalysts by Shi and his group.[24]

Following on from the pioneering work of Grigg and coworker on α-alkylation,[25] hydrogen borrowing has been actively examined by a number of research groups. Zhu et al. applied a Ru(II) complex encompassing an NNN pincer ligand[26] as a catalyst for α-alkylation of a variety of ketones with alcohols. Glorius and co-workers[27] described the synthesis of donepezil drug by α-alkylation of methylene ketones using a ruthenium(II) NHC catalyst. Chen's group[28] reported ruthenium pyridonate catalysts for α-alkylation of ketones with TOF values up to 3680. Our laboratory has also had success using ruthenium carbonyl complexes as catalysts[29] to link a variety of amines, diamines, and alcohols together. Although a few of the catalysts reported have good catalytic activity, the majority of them needed a long reaction time,, high temperatures, and a time-consuming workup technique, among other things, and had difficulties in the separation from the products. To overcome these disadvantages, the design of novel catalysts is desirable in the development of sustainable chemistry.

In general, it is acknowledged that the type of the ligand has a significant impact on coordination chemistry and frequently plays a key role in the activation of efficient homogeneous catalytic activities. In this connection, α-diimine ligands have been shown to stabilize organometallic complexes for a long time.[30] They are obtained by combining 2 equiv of a diketone with 2 equiv of an alkyl or aryl amine, typically catalyzed by a Lewis or Brønsted acid. The changeable backbone and aryl substituent in these synthetic pathways allow varying the steric and electronic effects at the metal core.

Following these overall considerations, we have chosen to concentrate on the synthesis of a group of α-diimine ligands with acenaphthenequinone and hydrazine in which different terminal substituents influence the properties of the metal center. Besides, the broad π arrangement of the acenaphthene ring joined with the amine moiety gives a wide scope of π-acceptor structures, offering exact command over the steric, optical, and electronic properties. The synthesized ligands were reacted with Ru(II) precursors to synthesize new Ru(II) catalysts. The coordination behavior of the ligands in the new complexes was studied by microanalyses, spectroscopic methods (IR, UV−vis, (^{1}H and ^{13}C) NMR, ESI-MS), and single-crystal XRD analysis. The catalytic efficiency of the new complexes was examined in the synthesis of new organic compounds via N-alkylation, α-alkylation, and β-alkylation reactions.

RESULTS AND DISCUSSION

The α-diimine hydrazone ligands $\mathbf{L_{1-3}}$ were synthesized from acenaphthenequinone and benzhydrazide, 2-thiophene carboxylic acid hydrazide, or isonicotinohydrazide in ethanol. The reaction between $[RuHCl(CO)(EPh_3)_3]$ (E = P or As) and the α-diimine hydrazone ligands ($\mathbf{L_{1-3}}$) in $CHCl_3$-EtOH leads

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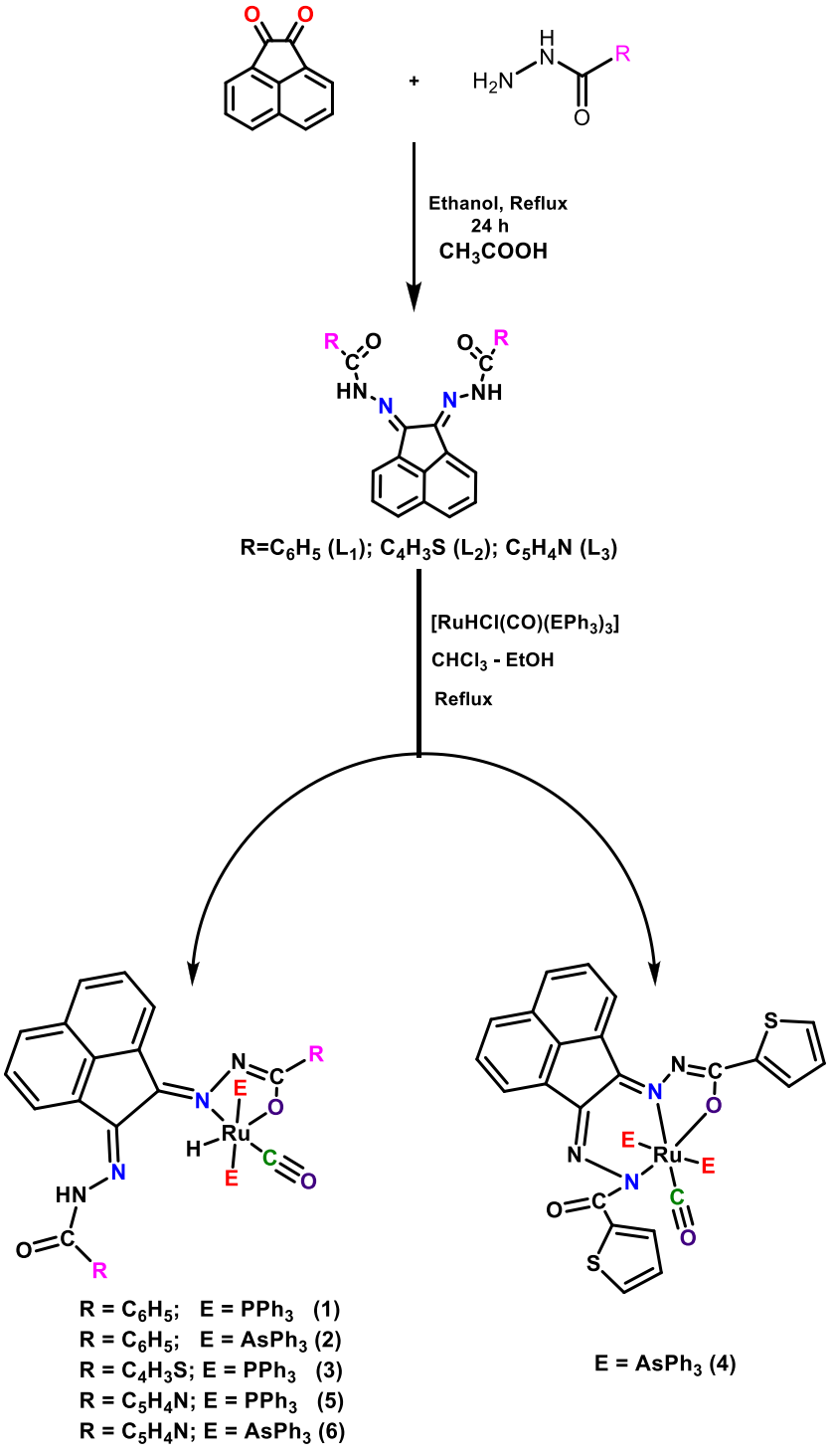
Scheme 1. Synthesis of the Ligands L_{1-3} and the Corresponding Ruthenium(II) Complexes 1−6



to the emergence of the new complexes (Scheme 1). The ligands and ruthenium complexes were identified by microanalysis, FT-IR, UV−vis, ^{1}H NMR, ^{13}C NMR, and mass spectroscopic methods. The molecular structures of the ligand and complexes (L_1, **1**, **3**, and **4**) were confirmed by the X-ray diffraction method. The entirety of the ligands and complexes are stable in air; soluble in dichloromethane, chloroform, acetonitrile, benzene, dimethylsulfoxide, dimethylformamide, and tetrahydrofuran; and insoluble in diethylether. The composition information (C, H, N, and S) of the complexes (**1**−**6**) concurred well with the proposed molecular formulae. The ESI mass spectra of ligands L_{1-3} displayed the molecular ion peak pattern of $[M + H]^+$ at m/z = 419.15, 431.06, and 421.14, respectively, while those of the complexes (**2**, **4**, **5**, and **6**) showed the $[M]^+$ peak at m/z = 1159.11, 1171.02, 1074.22, and 1161.99. Complexes **1** and **3** displayed the $[M + H]^+$ peak at m/z = 1073.23 and 1085.14, respectively. The ESI spectra and calculated isotopic distribution patterns for complexes **1**−**6** are in good accordance with the obtained spectra (see the Supporting Information, Figures S1−S9).

The infrared spectra of the ligands and new metal hydrazone complexes were determined to identify the presence of

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functional groups (see the Supporting Information, Figures S10−S18). In the spectra of the free ligands and their complexes (**1**−**3**, **5**, **6**), the N−H stretching frequency was in the range 3236−3167 cm^{-1}. The absorption band appearing at 1688−1659 cm^{-1} was assigned to $\upsilon_{(C=O)}$ vibration. A strong vibration was seen at 1596−1519 cm^{-1} corresponding to the imine group. Apart from the above absorptions, the peak that appeared at 1576−1479 cm^{-1} in the spectra of all complexes was assigned to the coordinated imine group. In addition, the appearance of a new band at 1297−1261 cm^{-1} due to $\upsilon_{(C-O)}$ indicates the coordination of the oxygen atom after enolization followed by deprotonation.[31] All of the complexes have a medium to strong band in the region 1944−1932 cm^{-1}, which is attributed to the terminally coordinated carbonyl group (C≡O), appearing at a somewhat higher frequency than the precursor complexes.[32] In the spectra of the complexes, the distinctive absorption bands due to PPh_3/$AsPh_3$ were also observed in the predicted regions.[33,34]

The electronic spectra of the complexes were obtained in a chloroform solution in the range 200−800 nm (see the Supporting Information, Figures S19−S27) and displayed three intense absorption bands at 250−560 nm. In the complexes' spectra, the presence of a band in the region 260−327 nm was designated as a ligand centered (LC) transition.[35] The shoulder appearing in the region 350−396 nm was assigned to the ligand to metal charge transfer (LMCT) transitions.[36] Moreover, the band due to d−d transition was observed in the range 450−552 nm for all the complexes. The electronic spectra of all the complexes are consistent with a six-coordination environment and also similar to reported octahedral ruthenium complexes.[37]

Further, the coordination mode of the ligand to ruthenium was confirmed by the ^{1}H NMR spectra (see the Supporting Information, Figures S28−S36). In the ^{1}H NMR spectra of all the ligands, the hydrazine N−H protons emerged as singlets around 12.34−12.11 ppm,[38] whereas in the spectra of complex **4**, this peak disappeared due to deprotonation of the amide nitrogen as well as enolization followed by deprotonation at the oxygen atom and coordination via N and O. However, in the spectra of the complexes **1**−**3**, **5**, and **6**, the N−H peak does not disappear and is shifted downfield at 16.28−16.17 ppm, revealing the noninvolvement of the N−H moiety. The peak at −13.44 to −12.41 ppm in the spectra of complexes **1**−**3**, **5**, and **6** was assigned to the hydride proton. Moreover, the signals due to the aromatic rings protons are observed at 8.70−6.91 ppm in all the ligands and complexes.

The formation of the proposed complexes is further supported by the ^{13}C NMR spectra of complexes (**1**−**6**), which show the expected signals in the right locations (see the Supporting Information, Figures S37−S42). The emergence of a peak at 207.1−195.4 ppm in the spectra of the complexes suggests the presence of a coordinated terminal carbonyl ligand. The peaks that appeared around 159.1−156.0 and 155.2−149.0 ppm in the spectra of complexes (**1**−**6**) were assigned to coordinated and uncoordinated imine carbons, respectively. The resonance due to N=C−O carbon occurred at 165.6−160.0 ppm. In addition, a signal was observed around 181.2−169.6 ppm due to the free amide carbonyl (C=O) carbon of the ligand. Moreover, the signals corresponding to the carbons of aromatic moieties of the complexes were observed in the range 141.8−126.5 ppm.[39]

X-ray Crystallographic Studies. The molecular structures of L_1 and ruthenium hydrazone complexes [Ru(H)(CO)$(PPh_3)_2(L_1)$] (**1**), [Ru(H)(CO)$(PPh_3)_2(L_2)$] (**3**), and [Ru(CO)$(AsPh_3)_2(L_2)$] (**4**) were solved by the single-crystal X-ray diffraction technique. The details of crystallographic data collected and structure solution with refinement are reported in the Experimental Section, and the results are presented in Tables S1 and S2 (see the Supporting Information). Single crystals of ligand $\mathbf{L_1}$ were grown in ethanol. They crystallized in a monoclinic crystal system with space group *Cc*. Crystals of complexes **1** and **3** were obtained from chloroform−ethanol, whereas those of complex **4** were from chloroform−acetonitrile solvents. The results reveal that complexes **1** and **3** formed in a monoclinic system with the space group $P2_1/c$, whereas complex **4** crystallized in a triclinic system with the space group *P*-1. The ORTEP views of complexes **1**, **3**, and **4** are shown below (Figures 2−4). In complexes **1** (Figure 2) and **3** (Figure 3), the hydrazine ligand coordinated as monobasic bidentate N, O donors with ruthenium via carbonyl oxygen and hydrazine nitrogen to form a five-membered chelate ring. In addition, a CO (*trans* to the imine nitrogen), a hydride, and two triphenylphosphine ligands are coordinated to the ruthenium center. The coordination sphere is similar, and the general structural motifs differ only in the terminal substitution (R = C_6H_5 or C_4H_3S). In complex **4** (Figure 4), the coordination geometry around the Ru(II) ion is a distorted octahedral, and the ruthenium atom is bounded to monobasic tridentate hydrazone donor molecules in such a way that five- and six-membered rings formed. The remaining site is

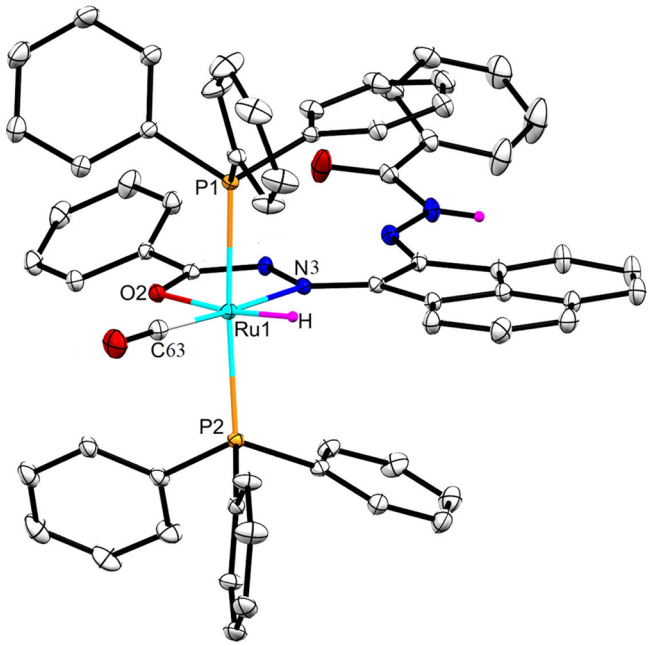

Figure 2. ORTEP view of complex **1** with 20% probability. Hydrogen atoms are omitted for clarity. Bond angles around Ru(II) ion: C(63)-Ru(1)-O (2) = 99.48 (11)°, C(63)-Ru(1)-N (3) = 174.31 (11)°, C(63)-Ru(1)-P (1) = 89.28 (11)°, C(63)-Ru(1)-P (2) = 92.09 (11)°, C(63)-Ru(1)-H = 82.6 (7)°, O(2)-Ru(1)-H = 175.9 (7)°, O(2)-Ru(1)-P (1) = 91.71 (6)°, O(2)-Ru(1)-P (2) = 91.86 (6)°, O(2)-Ru(1)-N (3) = 74.84 (7)°, N(3)-Ru(1)-P (1) = 91.30 (6)°, N(3)-Ru(1)-P (2) = 87.71 (6)°, N(3)-Ru(1)-H = 103.1 (6)°, P(1)-Ru(1)-H = 91.8 (7)°, P(2)-Ru(1)-H = 84.5 (7)°, and P(2)-Ru(1)-P (1) = 175.91 (2)°. Bond lengths: Ru(1)-C(63) = 1.840 (4) Å, Ru(1)-O (2) = 2.1312(18) Å, Ru(1)-H = 1.781(19) Å, Ru(1)-N (3) = 2.183 (2) Å, Ru(1)-P (1) = 2.3652 (8) Å, and Ru(1)-P (2) = 2.3770 (8) Å.

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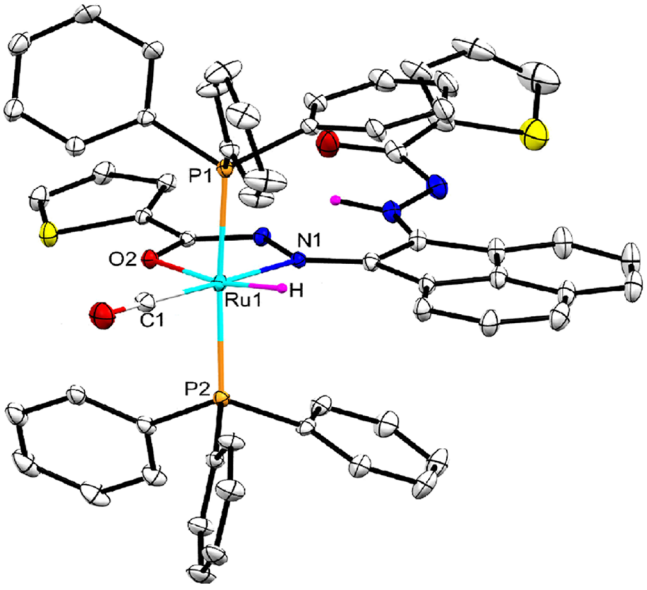

Figure 3. ORTEP view of complex **3** with 20% probability. Hydrogen atoms are omitted for clarity. Bond angles around Ru(II) ion: C(1)-Ru(1)-O (2) = 99.49 (19)°, C(1)-Ru(1)-N (1) = 174.41 (19)°, C(1)-Ru(1)-P (1) = 92.67 (17)°, C(1)-Ru(1)-P (2) = 88.04 (17)°, C(1)-Ru(1)-H = 84.9 (11)°, O(2)-Ru(1)-H = 170.3 (10)°, O(2)-Ru(1)-P (1) = 91.41 (9)°, O(2)-Ru(1)-P (2) = 92.37 (9)°, N(1)-Ru(1)-P (1) = 88.42 (10)°, N(1)-Ru(1)-P (2) = 91.26 (10)°, N(1)-Ru(1)-H = 100.7 (10)°, P(1)-Ru(1)-H = 78.8 (10)°, P(2)-Ru(1)-H = 97.3 (10)°, and P(2)-Ru(1)-P (1) = 175.98 (4)°. Bond lengths: Ru(1)-C (1) = 1.873 (6) Å, Ru(1)-O (2) = 2.134 (3) Å, Ru(1)-H = 1.76 (3) Å, Ru(1)-N (1) = 2.186 (4) Å, Ru(1)-P (1) = 2.3634(12) Å, and Ru(1)-P (2) = 2.3658(12) Å.

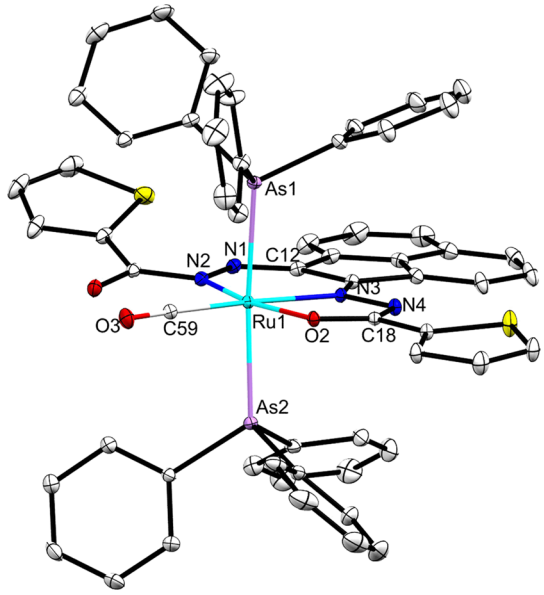

Figure 4. ORTEP view of complex **4** with 20% probability. Hydrogen atoms are omitted for clarity. Bond angles around Ru(II) ion: C(59)-Ru(1)-O (2) = 95.69 (11)°, C(59)-Ru(1)-N (2) = 96.62 (12)°, C(59)-Ru(1)-N (3) = 172.09 (12)°, C(59)-Ru(1)-As (1) = 90.24 (9)°, C(59)-Ru(1)-As (2) = 91.41 (9)°, O(2)-Ru(1)-As (1) = 86.19 (6)°, O(2)-Ru(1)-As (2) = 88.84 (6)°, N(3)-Ru(1)-N (2) = 91.27 (10)°, N(3)-Ru(1)-O (2) = 76.44 (8)°, N(3)-Ru(1)-As (1) = 90.05 (7)°, N(3)-Ru(1)-As (2) = 87.65 (7)°, N(2)-Ru(1)-O (2) = 167.52 (9)°, N(2)-Ru(1)-As (1) = 91.71 (7)°, N(2)-Ru(1)-As (2) = 92.89 (7)°, and As(2)-Ru(1)-As (1) = 174.904 (14)°. Bond lengths: Ru(1)-C(59) = 1.869 (3) Å, Ru(1)-O (2) = 2.082(19) Å, Ru(1)-N (2) = 2.080 (2) Å, Ru(1)-N (3) = 2.056 (2) Å, Ru(1)-As (1) = 2.4730 (4) Å, and Ru(1)-As (2) = 2.4778 (4) Å.

occupied by triphenylarsine, and the coordination sphere is different from the one of complexes **1** and **3**. In the structure of complexes **1** (Figure 2) and **3** (Figure 3), the *cis* angles N(3)-Ru(1)-P (1) = 91.30 (6)° and C(63)-Ru(1)-P (1) = 89.28 (11)° are acute, whereas the other *cis* angles P(1)-Ru(1)-H = 91.8 (7)°, N(3)-Ru(1)-P (2) = 87.71 (6)°, C(63)-Ru(1)-H = 82.6 (7)°, O(2)-Ru(1)-N (3) = 74.84 (7)°, and C(1)-Ru(1)-O (2) = 99.48 (11)° are obtuse. The *trans* angle values are found to be P(1)-Ru(1)-P (2) = 175.91 (2)°, O(2)-Ru(1)-H = 175.9 (7)°, and C(63)-Ru(1)-N (3) = 174.31 (11)° (for **1**) and of the complex **3** are the *cis* angles N(1)-Ru(1)-P (1) = 88.42(10)° and C(1)-Ru(1)-P (1) = 92.67 (17)° are acute, whereas the other *cis* angles P(1)-Ru(1)-H = 78.8 (10)°, N(1)-Ru(1)-P (2) = 91.26(10)°, C(1)-Ru(1)-H = 84.9 (11)°, and O(2)-Ru(1)-N (1) = 74.99 (12)°, C(1)-Ru(1)-O (2) = 99.49(19)° are obtuse. The *trans* angle values are present to be P(1)-Ru(1)-P (2) = 175.98 (4)°, O(2)-Ru(1)-H = 170.3(10)°, and C(1)-Ru(1)-N (1) = 174.41 (19)°. These values are comparable with similar complexes reported previously.[40,41]

In complex **4** (Figure 4), the Ru(II) ion displays six-coordination with an octahedral geometry wherein a tridentate mode creates five- and six-membered chelate rings involving N_{imine}, O_{amide}, and N_{amide}. The remaining apical sites are filled up by carbonyl and a pair of $AsPh_3$ co-ligands based on the CN_2OAs_2 coordination environment. The *cis* angles As(2)-Ru(1)-N (2) = 92.90 (7)° and As(1)-Ru(1)-C(59) = 91.3 (1)° are acute, whereas other the *cis* angles O(2)-Ru(1)-C(59) = 95.6 (1)°, N(3)-Ru(1)-O (2) = 76.45 (9)°, N(2)-Ru(1)-C(59) = 96.6(1)°, N(2)-Ru(1)-N (3) = 91.3(1)°, As(2)-Ru(1)-O (2) = 88.87(1)°, and As(2)-Ru(1)-N (3) = 87.66(7)° are obtuse. The *trans* angles As(2)-Ru(1)-As (1) = 174.90 (2)°, N(3)-Ru(1)-C(59) = 172.0 (1)°, and O(2)-Ru(1)-N (2) = 167.56 (9)° deviate from linearity. The As (1)−Ru−As (2) angle in complex **4** is 174.90, which reveals that the two $AsPh_3$ ligands are almost vertically situated at the two sides of the ligand plane (*trans* to each other).[42,43]

The ruthenium catalyzed *N*-alkylation of benzylamine with benzyl alcohol was selected as a model reaction. Several reactions were tried to optimize the reaction conditions, and results are arranged in Table 1. In most of the catalytic reactions, the solvents play an important role in controlling the catalytic activities of the catalyst used. Hence, at the start of our studies, the solvent dependent differences in catalyst activity in the presence of KOH as base were explored using solvents toluene, benzene, *o*-xylene, CH_3CN, 1,4-dioxane, THF, DMSO, DMF, and EtOH. Aromatic hydrocarbon solvents such as toluene and benzene (Table 1; entries 1 and 2) afford better yields; especially toluene gives an excellent yield (up to 97%). Changing the solvent to polar aprotic (DMSO, DMF) or protic (EtOH) furnishes the desired product in moderate yield (Table 1, entries 7−9). Interestingly, when the reaction was done in THF, no reaction occurs (Table 1, entry 6). Likewise, no reaction occurs when the reaction is carried out in the absence of a solvent (Table 1, entries 10).The presence of acetonitrile or 1,4-dioxane gives a moderate yield (Table 1, entries 4 and 5). The results in Table 1 reveal that toluene is the best choice of solvent. The N-alkylation reaction was further performed in toluene at

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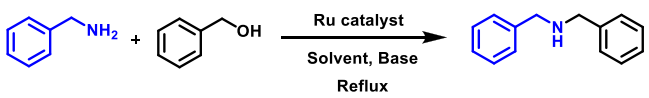
Table 1. Optimization of Reaction Parameters[a]



entry	catalyst	solvent	base	amount of catalyst (mol %)	T (°C)	time (h)	yield (%)[b]
1[c]	3	toluene	KOH	0.5	110	12	97
2	3	benzene	KOH	0.5	72	12	65
3	3	xylene	KOH	0.5	146	12	11
4	3	CH_3CN	KOH	0.5	83	12	53
5	3	dioxane	KOH	0.5	101	12	72
6	3	THF	KOH	0.5	70	12	trace
7	3	DMSO	KOH	0.5	190	12	18
8	3	DMF	KOH	0.5	160	12	15
9	3	ethanol	KOH	0.5	82	12	66
10[d]	3		KOH	0.5	110	24	trace
11	3	toluene	KOH	0.5	RT	12	trace
12	3	toluene	KOH	0.5	90	12	58
13	3	toluene	KOH	0.5	100	12	72
14	3	toluene	Na_2CO_3	0.5	110	12	16
15	3	toluene	K_2CO_3	0.5	110	12	19
16	3	toluene	Cs_2CO_3	0.5	110	12	25
17	3	toluene	NaOH	0.5	110	12	59
18	3	toluene	NaO^{t}Bu	0.5	110	12	33
19	3	toluene	KO^{t}Bu	0.5	110	12	56
20[e]	3	toluene		0.5	110	12	trace
21	3	toluene	KOH	0.15	110	12	62
22	3	toluene	KOH	0.25	110	12	74
23	1	toluene	KOH	0.5	110	12	84
24	2	toluene	KOH	0.5	110	12	88
25	3	toluene	KOH	0.5	110	12	80
26	4	toluene	KOH	0.5	110	12	81
27[f]		toluene	KOH		110	12	trace

[a]Reaction conditions: 5.0 mmol of benzyl amine, 5.0 mmol of benzyl alcohol, 0.5 mol % of the catalyst, and 5.0 mol % of the base under reflux. [b]Isolated yields for addition of the product. [c]Optimal reaction conditions. [d]Without solvent. [e]Without base. [f]No catalyst.

different temperatures (90−110 °C), with the finding that 110 °C is the optimum temperature for the alkylation of amines (Table 1, entry 1). Moreover, the optimization results reveal that 12 h is required for the maximum conversion of the product.

Subsequently, the reaction conditions were optimized through different bases such as Na_2CO_3, K_2CO_3, Cs_2CO_3, NaOH, NaO^{t}Bu, KO^{t}Bu, and KOH, and the results are given in Table 1. In the absence of a base (Table 1, entry 20), the catalytic reaction was unsuccessful. Moderate bases such as Na_2CO_3, K_2CO_3, and Cs_2CO_3 were less reactive (Table 1, entries 14−16). The reaction was expedited moderately by the inclusion of strong bases such as NaOH, NaO^{t}Bu, and KO^{t}Bu (Table 1, entries 17−19). However, the presence of KOH accelerates the reaction the most, and the yield of N-alkylated amine was excellent (Table 1, entry 1 up to 97%). Hence, KOH was chosen as the ultimate choice of base to precede the N-alkylation reactions.

Further, the optimum catalyst among the synthesized complexes and amount of catalyst required for maximum yield of the product were screened. The results are presented in Table 1. The results reveal that when 0.5 mol % of the catalyst was used, ruthenium hydrazone complexes containing thiophene moiety as a terminal substituent led to a higher yield than those containing benzene or pyridine moiety. This behavior indicates that electronic effects or reactivity of the terminal substituent plays an important role in the catalytic efficiency. In conclusion, it is observed that complex **3** containing terminal five-membered thiophene and triphenylphosphine co-ligands shows a higher catalytic activity toward the synthesis of amines under optimized conditions with good yield compared to other catalysts.[44] Hence, complex **3** was chosen as the precatalyst for the C−N bond formation reaction.

N-Alkylation of amines with alcohols provides an efficient route to new secondary amines and can therefore be a crucial step in the atom economical synthesis of pharmaceutically significant molecules.[45] It is critical for any new catalyst development in this field to demonstrate its broad application. Various aromatic amines as well as aliphatic amines with alcohols were tested under optimum circumstances to illustrate the use of our unique catalytic system (Table 2). The alkylation of aniline with benzyl alcohol produced the secondary amine product 6a with isolated yields of 93%. Benzyl amine underwent alkylation smoothly with benzyl alcohol to give 6b in excellent yields (95%). Using benzyl alcohol, alkylation of 2,4,6-trimethyl aniline, 2,6-dimethyl amine, 2,6-diethyl amine, and diisopropyl aniline was achieved in 90% (6c), 88% (6d), 81% (6e), and 79% (6f) yields, respectively, at 110 °C. Up to 75% yield was obtained for the secondary amine 6g when alkylation of cyclohexylamine was carried out using benzyl alcohol. Subsequently, very good yields of corresponding alkylated amine products were obtained for alkylation of heteroaromatic amine (6 h, 87%), aliphatic amines, and aliphatic diamines (entries 6i, 6j, 6k, and 6l) using benzyl alcohol as the alkylating agent. Moreover, good yields of products were acquired (6m 79%, 6n 81%) for the alkylation of 1-naphthylamine and 4-methoxy aniline using the relatively easily oxidizable benzyl alcohol at 110 °C. Under the present catalytic system, benzyl alcohol can also be used as the alkylating agent for piperidine and 2-aminopyridine as substrates and form the products up to 88% (6o) and 78% (6p) yields. The congeniality of the catalytic system with heterocyclic diamine was demonstrated, and a very good result (6q) was obtained utilizing catalyst **3** for the *N,N′*-dialkylation of 2,6-diaminopyridine with benzyl alcohol. The required 2-substituted benzimidazole was obtained in 70% isolated yield by reacting *o*-phenylenediamine with benzyl alcohol (6r).

The scope of the α-alkylation reaction was investigated with respect to aromatic ketones and alcohols. Preliminary reactivity tests were conducted using acetophenone and benzyl alcohol as substrates and complex **3** as a catalyst. After encouraging results, the alkylation reaction was extended to various substituted ketones and alcohols. The results are summarized in Table 3. Differently substituted benzyl alcohols were used as co-substrates for the indicated reactions under the standard conditions, and in most cases, using benzyl alcohols bearing electron-withdrawing or -donating groups, the desired ketone products (Table 3, entries 7a−7c) were isolated with good to excellent yields. When the reaction was conducted between acetophenone and electron-rich 1-phenyl ethanol, the product 1,3-diphenyl butan-1-one formed in moderate yield (Table 3, entry 7d, 89%). Subsequently, *o*-hydroxy acetophenone underwent alkylation smoothly to form new ketones in 95−90% yields (Table 3, entries 7e−7h). Using 4-methoxy-2-hydroxy acetophenone as the substrate, the alkylation of

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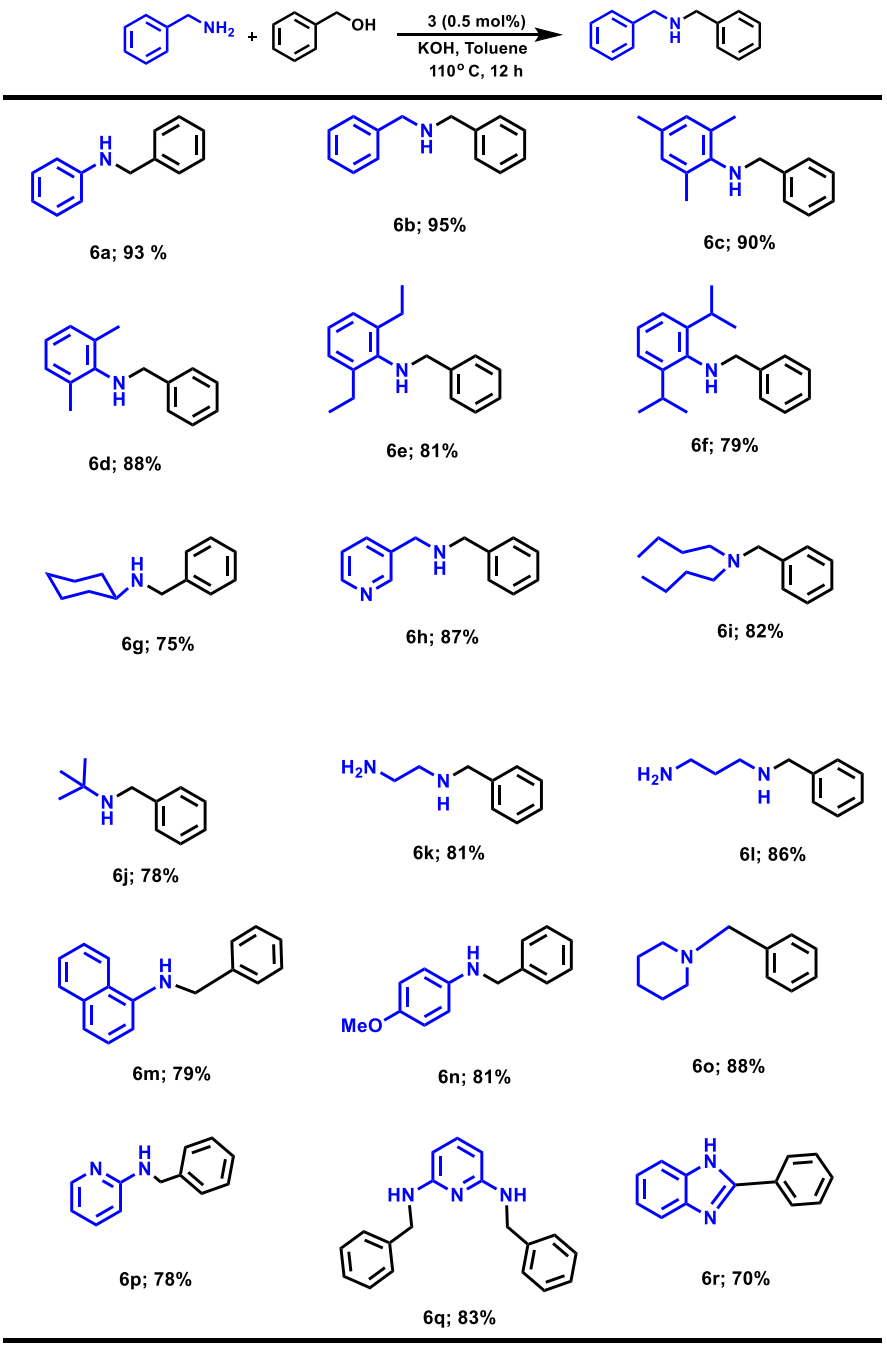
Table 2. N-Alkylation of Various Substituted Amines with Benzyl Alcohol under Optimized Conditions[a,b]



[a]Reaction conditions: 5.0 mmol of benzyl amine, 5.0 mmol of benzyl alcohol, 0.5 mol % of catalyst **3**, and 5.0 mol % of the base at 110 °C for 12 h. [b]Isolated yields.

substituted alcohols was also explored (Table 3, entries 7i−7l). However, the yield of the products was slightly lower than that of unsubstituted and *o*-hydroxy substituted ketones.

Next, employing a range of secondary alcohols, the substrate scope was extended to the β-alkylation reaction under optimal conditions, and the protocol generality was investigated (Table 4). Unsubstituted and substituted benzyl alcohol containing an electron-donating methoxy and methyl substituent interacted with 1-phenyl ethanol to form the desired products in excellent yields (Table 4, entries 8a−8c, 96−98%). The use of long-chain aliphatic alcohol for alkylation with 1-phenyl ethanol led to the desired product in 65% yield (Table 4, entry 8d). The reaction of the above aromatic secondary alcohols with 2-butanol afforded the corresponding products in moderate yield (Table 4, entries 8e−8g, 89−82%). Aliphatic pentanol underwent the reaction with 2-butanol to form the product (Table 4, entry 8h) in 68% yield.

A plausible mechanism for Ru(II) α-diimine hydrazone complex **3** catalyzed N-alkylation and α-alkylation was proposed based on previous reports (Scheme 2).[46,47] Initially, alcohol is coordinated to the metal with loss of PPh_3 in the presence of the base to form a Ru-alkoxide species, which undergoes β-hydrogen elimination reaction to form a hydrido ruthenium species and aldehyde in the second step. For the N-

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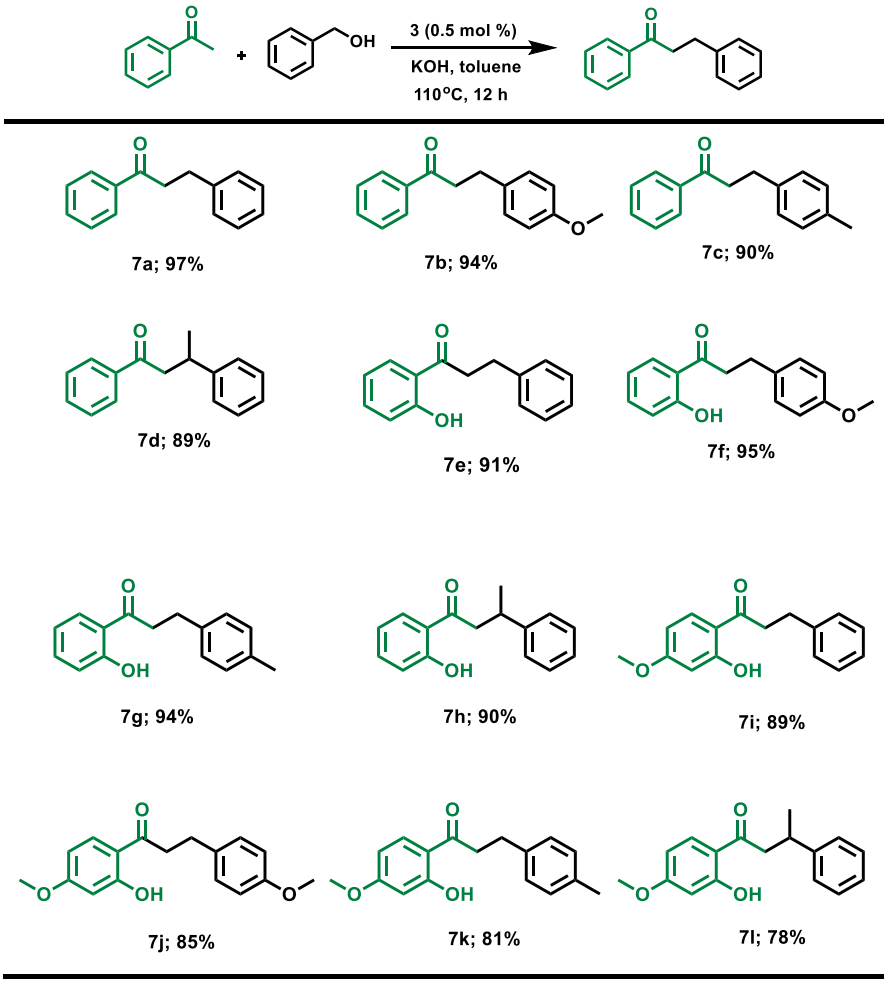
Table 3. Ru(II)-Catalyzed α-Alkylation of Ketones with Primary alcohols[a,b]



[a]Reaction conditions: 1.0 mmol of ketone, 1.0 mmol of primary alcohol, 0.5 mol % of catalyst **3**, and 5.0 mol % of the base at 110 °C for 12 h. [b]Isolated yields.

alkylation process, in the final step, the dehydrative condensation and insertion processes occur simultaneously followed by alcoholysis of the resulting (amido)-ruthenium species, affording the N-alkylation product and reproducing the catalyst as well as completing the catalytic cycle.

In the α-alkylation process, the aldehyde formed in the second step undergoes cross-aldol condensation with ketone to give an α,β-unsaturated ketone. Finally, the coordination and addition of Ru-H species into the double bond of the α,β-unsaturated ketone followed by alcoholysis afford the ketone product with the regeneration of catalyst. The β-alkylation of secondary alcohols with primary alcohols undergoes a similar mechanism as per the α-alkylation reaction.

Control Experiments. According to previously published hydrogen transfer mechanisms,[48−51] it is anticipated that the N-alkylation process goes through three steps, viz., alcohol oxidation, imine production, and imine hydrogenation. A few trials were conducted to confirm it. The oxidation of benzyl alcohol to benzaldehyde was seen in the absence of amine. Under the current reaction conditions, the first step is confirmed (Scheme 3a). When the reaction was carried out at a low temperature (70 °C) or stopped in-between, imine was observed as the major product, which confirms the second step. Under the current reaction conditions, hydrogenation of the imine yielded the corresponding amine, confirming the second step (Scheme 3b), and the result was confirmed by ^{1}H NMR spectroscopy (see the Supporting Information, Figure S45). Subsequently, we examined the α-alkylation reaction between ketone and alcohol proceeding through the chalcone intermediate, which was well established by previous literature methods.[52−54] In our case, the intermediate has been obtained by the reaction of ketone and alcohol under a similar catalytic condition after 12 h (Scheme 4). Further, the formation of the intermediate was evidenced by ^{13}C NMR with the conversion of 71% of a desired chalcone. This result shows that the ruthenium complex is not just catalyzing the borrowing hydrogen steps (dehydrogenation of the primary alcohol and hydrogenation of the aldol condensation product) but is also associated with the crucial C−C bond forming condensation reaction.

At this juncture, the present catalyst is compared with few reported catalytic systems in terms of catalyst loading, reaction conditions, and yields of product formation to reveal the advantages. The palladium catalyst reported by Dang et al. for the N-alkylation of aniline using benzyl alcohol gave up to 80% yield of the desired secondary amine product at 180 °C.[55] The Ru catalyst of Enyong and Moasser required 4 mol % catalytic loading and a longer reaction time for formation of products

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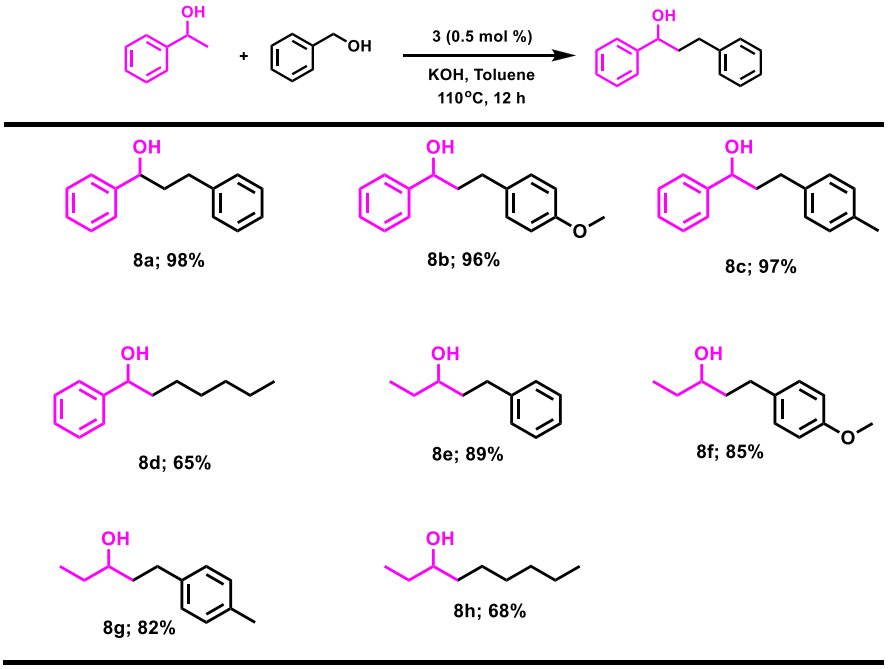
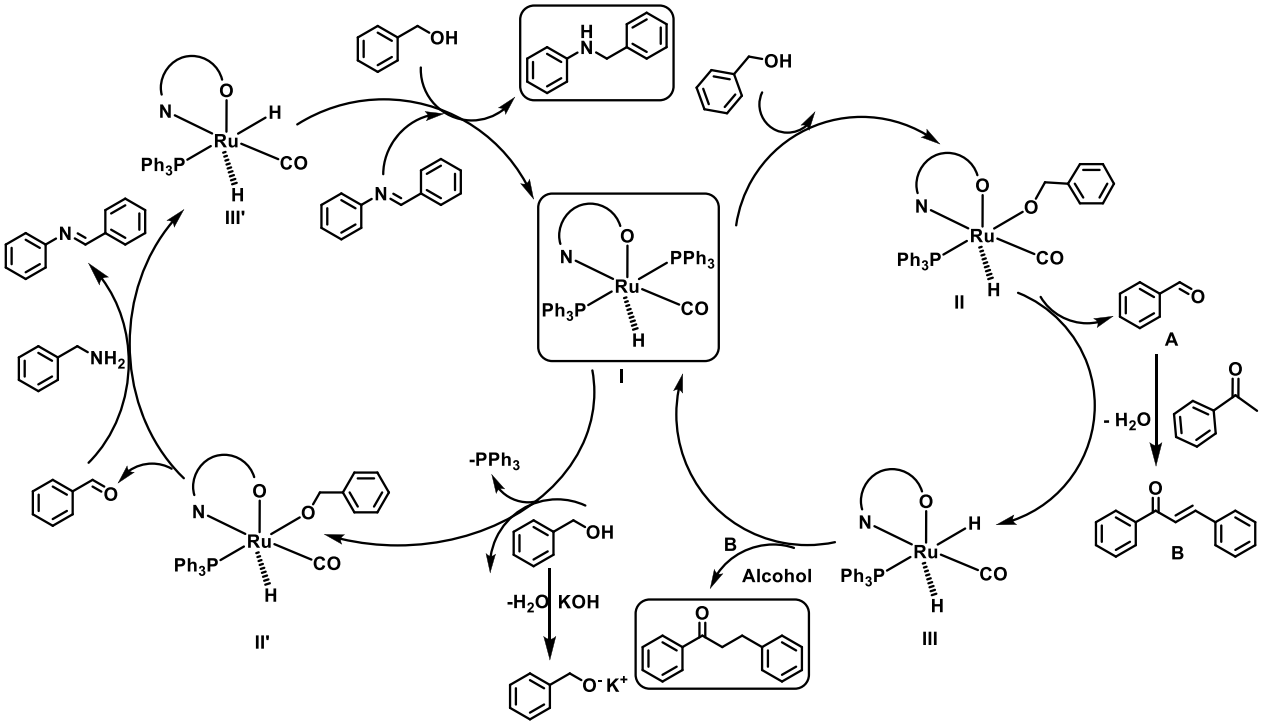
Table 4. Ru(II)-Catalyzed β-Alkylation of Secondary Alcohols with Primary Alcohols[a,b]



[a]Reaction conditions: 2.5 mmol of secondary alcohol, 2.5 mmol of primary alcohol, 0.5 mol % of catalyst **3**, and 5.0 mol % of the base at 110 °C for 12 h. [b]Isolated yields.

Scheme 2. Plausible Catalytic Cycle for the N-Alkylation and α-Alkylation Reaction



up to 85% yield at 110 °C.[56] The Ru NHC catalyst[57] required 1 mol % catalyst loading and 24 h reaction time at 120 °C for the effective formation of N-alkylated products. Zhang et al. disclosed the cobalt catalyzed (2 mol %) N-alkylation of amines with alcohols in a long reaction time (48 h).[58] The catalytic performance of the [$RuCl_2(\eta^6$-*p*-cymene) (NHC)] catalyst (1.5 mol %)[59] was efficient only after 20 h at 120 °C.[59]

Mn catalyzed α-alkylation processes reported by Gunanathan and Milstein required a lot of catalyst (1−2 mol %), high temperature (125−140 °C), and longer time (18−24 h) to complete the reactions. The Ru NHC catalyst[60] needs 2 mol % catalyst loading and 24 h reaction time at 100 °C for the formation of ketones. The catalytic performance of the $[RuCl_2(\eta^6$-*p*-cymene$)]_2$ and P,N ligand catalyst[61] was effective only after 18 h at 120 °C. An inert atmosphere was required by

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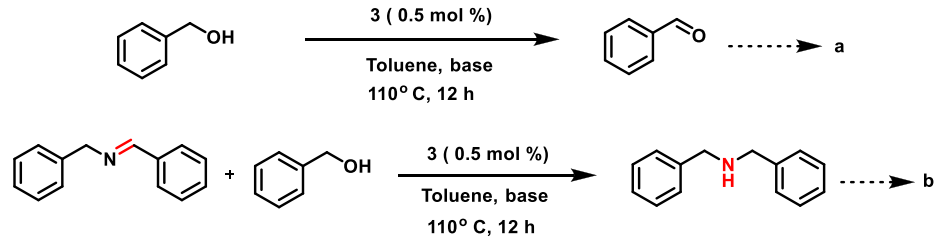
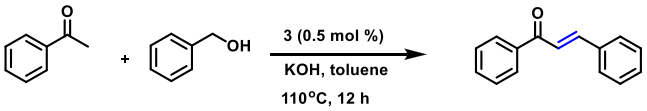
Scheme 3. Control Experiments for N-Alkylation: (a) Oxidation of Alcohol and (b) Hydrogenation of Imine



Scheme 4. Control Experiment for C−C Coupling of Alcohols



NNN pincer Ru(II) complexes and ruthenium pyridonate complexes[27,28] for effective α-alkylation process. The α-alkylation of 1-phenylethanol with benzyl alcohol catalyzed by ruthenium complexes required a nitrogen environment for optimal product formation.[28] Similarly, a pyridyl-supported pyrazolyl-imidazolyl manganese complex needs a high amount of base (30 mol %, ^{t}BuOK)[62] for β-alkylation of secondary alcohols with primary alcohols. The catalytic performance of the Ru(III)-NNN complex bearing a pyridyl-supported pyrazolylimidazolyl ligand reveals that 1 mol % of the catalyst, 20 mol % of the base (KOH), and a nitrogen atmosphere are required for β-alkylation of secondary alcohols with primary alcohols.[63] It is worth noting that the simple conversion processes in the presence of our catalysts have a number of advantages over the previous approaches published. In comparison to other catalysts, the salient features of the titled catalysts include the following: (a) required optimum temperature and short time, (b) lower amount of the catalyst and base, (c) insensitivity to air, (d) no oxidant or additive needed, (e) broad substrate scope with excellent yields, and (f) simple workup process.

CONCLUSIONS

We have demonstrated the synthesis of a series of ruthenium complexes (**1**−**6**) with α-diimine hydrazone ligands. The structure of the complexes was determined by spectral studies including single-crystal XRD (for $\mathbf{L_1}$, **1**, **3**, and **4**). Based on the characterization results, an octahedral geometry was confirmed for all the complexes. The versatile Ru^{II} α-diimine hydrazone catalysts are very useful systems for the N-alkylation of amines with primary alcohols, the α-alkylation of ketones, and the β-alkylation of secondary alcohols in the presence of KOH/toluene. The present protocol does not require a N_2 atmosphere. Notably, complex **3** was found to be very efficient toward the alkylation reactions. This catalysis provides a clean, convenient, and practical route due to the readily available, cheap, and stable catalyst; smooth as well as effective formation of the products under mild conditions; and easy workup processes.

EXPERIMENTAL SECTION

General Considerations. Chemicals and solvents of analytical quality were obtained from Sigma-Aldrich and utilized without additional purification.[64] TLC was performed on Merck 1.05554 aluminum sheets that had been precoated with silica gel 60 F254, and the results were seen using a UV chamber (254 nm). The compounds were purified by column chromatography using a Merck silica mesh (100−200). A Bruker D8 Quest Eco diffractometer was used to record crystallographic data. A Vario EL III Elemental Analyzer was used to collect the analytical data (carbon, hydrogen, nitrogen, and sulfur). FT-IR spectra of the compounds were performed on a Bruker alpha FT-IR spectrophotometer in the range 4000−400 cm^{-1}. The UV−visible (200−800 nm) spectra were acquired using DMSO solvent on a Shimadzu UV-1800 spectrophotometer. The nuclear magnetic resonance spectra (^{1}H and ^{13}C) were obtained on a Bruker AV400 instrument using deuterated DMSO-d_6 or $CDCl_3$ and tetramethylsilane as solvent and an internal standard. A Q-TOF Micro Analyzer was used to quantify the molecular weight of substances using electrospray ionization. A melting point device from Lab India was used to determine the melting points. The synthetic procedure for α-diimine hydrazone ligands was slightly modified from the previously published one.[65] The direct procedure according to prior literature approaches[66,67] was employed in the synthesis of the ruthenium complexes $[RuHCl(CO)(PPh_3)_3]$ and $[RuHCl(CO)(AsPh_3)_3]$.

X-ray Crystallography. A single crystal of a suitable size ($\mathbf{L_1}$, **1**, **3**, and **4**) was mounted on the most elevated mark of a glass fiber and transferred to a Bruker D8 Quest Eco diffractometer. Information was gathered at 273 (2) K ($\mathbf{L_1}$), 296 (2) K (**1** and **4**), and 293 (2) K (**3**) utilizing monochromated Mo Kα radiation (λ = 0.71073 Å) by the APEX-III program suit;[68] further, the integration, Lorentz and polarization corrections, and merging of data were carried out using SAINT.[68] The absorption correction was performed by SADABS[68] by using the SORTAV software.[69] The hydrogen atoms of all C−H and N−H hydrogen bonds were located from the difference Fourier map and were refined anisotropically. The structure was solved by direct methods using SHELXS-2014[70] and refined by SHELXL-2014[71] programs incorporated to the WINGX package.[72] The triphenyl phosphine ligand in the crystal structure shows thermal disorder, and this was resolved by the WINGX software. The ORTEP[72] views of the molecule with displacement ellipsoids drawn at the 20% probability level are shown in the figures 2−4. The molecular and packing diagrams were generated using the software MERCURY.[73]

General Procedure for the Synthesis of α-Diimine Ligands. The α-diimine ligands ($\mathbf{L_{1-3}}$) were synthesized by reacting acenaphthenequinone and substituted hydrazide (1:2 molar ratio) in 20 mL of ethyl alcohol in the presence of 2 mL of acetic acid. The whole mixture was heated under reflux at 80 °C for 24 h, and the TLC plates were used to optimize the reaction. At the end of the reaction, all volatiles were taken out from the rotary evaporator, and the remaining residue was

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washed multiple times with ethanol. Finally, the product was vacuum dried.

*Acenaphthylene-1,2-diylidene Di(benzohydrazide) (**L**$_1$).* **L**$_1$ was synthesized using acenaphthenequinone (1 mmol, 0.1822 g) and benzhydrazide (2 mmol, 0.418 g) by the general procedure. Color: yellow. Yield: 0.281 g, 78%. M.pt.: 260 °C. Anal. Calcd. for $C_{26}H_{18}N_4O_2$: C, 74.63; H, 4.34; N, 13.39%. Found: C, 74.19; H, 3.99; N, 12.96%. FTIR (ATR, ν cm^{-1}): 3186 (s), 3050 (N−H$_{hydrazide}$), 1688 (C═O), 1596 (C═N). UV−vis (DMSO, λ_{max} nm): 415, 369, 325. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 12.11 (s, 2H, N−H $_{hydrazide}$), 8.45 (d, 2H, J = 8.24 Hz, ArH), 8.21−8.10 (t, 2H, J = 7.25 Hz, ArH), 8.01 (d, 2H, J = 8.20 Hz, ArH), 7.91−7.86 (t, 2H, J = 7.12 Hz, ArH), 7.84−7.79 (t, 4H, J = 7.96 Hz, ArH),7.71 (d, 4H, J = 8.21 Hz, ArH). MS (ESI, m/z): calculated 418.46, found 419.15 [M + H]$^+$. The single crystals were grown in the mother liquid for X-ray diffraction analysis.

*Acenaphthylene-1,2-diylidene Bis(thiophene-2-carbohydrazide) (**L**$_2$).* **L**$_2$ was synthesized using acenaphthenequinone (1 mmol, 0.1822 g) and thiophene-2-carboxylic acid hydrazide (2 mmol, 0.430 g) by the general procedure. Color: yellow. Yield: 0.245 g, 80%. M.pt.: 130 °C. Anal. Calcd. for $C_{22}H_{14}N_4O_2S_2$: C, 61.38; H, 3.28; N, 13.01; S, 14.89%. Found: C, 61.07; H, 3.02; N, 12.51; S, 14.49%. FTIR (ATR, ν cm^{-1}): 3167 (s), 3072 (N−H$_{hydrazide}$), 1659 (C═O), 1519 (C═N). UV−vis (DMSO, λ_{max} nm): 425, 369, 327. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 12.12 (s, 2H, N−H$_{hydrazide}$), 8.41 (d, 2H, J = 8.24 Hz, ArH), 8.21−8.15 (t, 2H, J = 6.98 Hz, ArH), 8.11 (d, 2H, J = 8.92 Hz, ArH), 8.00 (d, 2H, J = 8.16 Hz, ArH),7.92 (d, 2H, J = 7.32 Hz, ArH), 7.88−7.83 (t, 2H, J = 3.92 Hz, Ar H). MS (ESI, m/z): calculated 430.50, found 431.06 [M + H]$^+$.

*Acenaphthylene-1,2-diylidene Di(isonicotinohydrazide) (**L**$_3$).* **L**$_3$ was synthesized using acenaphthenequinone (1 mmol, 0.1822 g) and isoniazide (2 mmol, 0.420 g) by the general procedure. Color: yellow. Yield: 0.215 g, 75%. M.pt.: 210 °C. Anal. Calcd. for $C_{24}H_{16}N_6O_2$: C, 68.56; H, 3.84; N, 19.99%. Found: C, 68.45; H, 3.45; N, 19.58%. FTIR (ATR, ν cm^{-1}): 3236 (s), 3032 (N−H$_{hydrazide}$), 1684 (C═O), 1527 (C═N); UV−vis (DMSO, λ_{max} nm): 426, 367, 322. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 12.12 (s, 2H, N−H$_{hydrazide}$), 8.42 (d, 2H, J = 8.10 Hz, ArH), 8.19 (d, 2H, J = 8.20 Hz, ArH), 8.12 (d,4H, J = 7.04 Hz, ArH), 8.05 (d, 4H, J = 7.48 Hz ArH),7.92−7.90 (t, 2H, J = 7.05 Hz, ArH). MS (ESI, m/z): calculated 420.43, found 421.14 [M + H]$^+$.

General Procedure for the Synthesis of Ruthenium(II) Complexes. [RuHCl(CO)(EPh$_3$)$_3$] (E = As or P) (0.1 mmol) and α-diimine ligands (0.1 mmol) were suspended in chloroform−ethanol solvent combination (20 mL, 1:1, v/v) and refluxed for 6 h at 80 °C with stirring. Thin layer chromatography (TLC) was used to confirm the formation of the complex, and the solvents were eliminated under vacuum. The crude product formed was rinsed many times with petroleum ether. The product was also purified using silica mesh column chromatography with a mobile phase of petroleum ether−ethyl acetate (8:2, v/v).

*[Ru(H)(CO)(PPh$_3$)$_2$(L$_1$)] (**1**).* [RuHCl(CO)(PPh$_3$)$_3$] (0.1 mmol, 0.0954 g) and **L**$_1$ (0.1 mmol, 0.0418 g) were used to synthesize complex **1**. Color: red-brown. Yield: 0.811 g, 76%. M.pt.: 88 °C. Anal. Calcd. for $C_{63}H_{48}P_2N_4O_3Ru$: C, 70.58; H, 4.51; N, 5.23%. Found: C, 70.18; H, 3.98; N, 4.82%. FTIR (ATR, ν cm^{-1}): 3046 (N−H$_{hydrazide}$), 1933 (C≡O), 1680 (C═O), 1563 (C═N), 1267 (C−O), 692 (Ru−P). UV−vis (DMSO, λ_{max} nm): 540, 396, 324. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): −12.92 (t, 1H, Ru−H), 16.27 (s, 1H, N−H$_{hydrazide}$), 8.90 (d, 2H, J = 7.10 Hz, ArH), 8.84 (d, 2H, J = 7.12 Hz, ArH), 8.63 (d, 4H, J = 6.92 Hz, ArH), 8.29−8.23 (t, 2H, J = 8.16 Hz, ArH), 8.11−8.06 (t, 2H, J = 7.32 Hz, ArH), 7.89−7.83 (t, 2H, J = 7.01 Hz, ArH), 7.81−7.73 (t, 3H, J = 7.20 Hz, ArH), 7.59−7.56 (m, 6H, ArH), 7.51−7.46 (m, 12H, ArH), 7.12−7.03 (m, 12H, ArH). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 203.09 (Ru−C≡O), 176.37 (C═O$_{hydrazide}$), 165.69 (C−O−Ru), 155.28 (C═N−Ru), 136.63 (ArC), 134.96 (ArC), 134.29 (ArC), 133.36 (ArC), 133.01 (ArC), 132.17 (ArC), 132.07 (ArC), 131.28 (ArC), 130.97 (ArC), 130.61 (ArC), 128.57 (ArC), 128.45 (ArC), 125.94 (ArC). MS (ESI, m/z): calculated 1072.12, found 1073.23 [M + H]$^+$. Slow evaporation of complex in 3:1 CHCl$_3$−EtOH solvent mixture yielded needle-shaped X-ray quality crystals of complex **1**.

*[Ru(H)(CO)(AsPh$_3$)$_2$(L$_1$)] (**2**).* [RuHCl(CO)(AsPh$_3$)$_3$] (0.1 mmol, 0.1054 g) and **L**$_1$ (0.1 mmol, 0.0418 g) were used to synthesize complex **2**. Color: red-brown. Yield: 0.811 g, 76%. M.pt.: 88 °C. Anal. Calcd. for $C_{63}H_{48}As_2N_4O_3Ru$: C, 65.23; H, 4.17; N, 4.83%. Found: C, 64.88; H, 3.64; N, 4.22%. FTIR (ATR, ν cm^{-1}): 3046 (N−H$_{hydrazide}$), 1937 (C≡O), 1633 (C═O), 1435 (C═N), 1264 (C−O), 689 (Ru−As). UV−vis (DMSO, λ_{max} nm): 541, 396, 327. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): −13.76 (s, 1H, Ru−H), 15.45 (s, 1H, N−H$_{hydrazide}$), 8.91−8.88 (t, 2H, J = 7.88 Hz, Ar H), 8.85 (d, 2H, J = 7.48 Hz, ArH), 8.74 (d, 2H, J = 8.76 Hz, Ar H), 8.18−8.15 (t, 4H, J = 8.48 Hz, Ar H), 8.05−8.00 (t, 2H, J = 4.36 Hz, Ar H), 7.95−7.90 (t, 2H, J = 5.78 Hz, Ar H), 7.72 (d, 2H, J = 8.10 Hz, Ar H), 7.63−7.55 (m, 12H, Ar H), 7.52−7.44 (t, 6H, J = 4.76 Hz, Ar H), 7.22−7.11 (m, 12H, Ar H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 202.01 (Ru−C≡O), 181.23 (C═O$_{hydrazide}$), 160.74 (C−O−Ru), 151.04 (C═N−Ru), 134.34 (Ar C), 134.29 (Ar C), 133.33 (Ar C), 132.96 (Ar C), 132.85 (Ar C), 132.22 (Ar C), 131.71 (Ar C), 130.83 (Ar C), 130.22 (Ar C), 129.75 (Ar C), 129.45 (Ar C), 128.45 (Ar C), 128.19 (Ar C), 127.70 (Ar C), 127.33 (Ar C). MS (ESI,m/z): calculated 1159.01, found 1159.11[M]$^+$.

*[Ru(H)(CO)(PPh$_3$)$_2$(L$_2$)] (**3**).* [RuHCl(CO)(PPh$_3$)$_3$] (0.1 mmol, 0.0954 g) and **L**$_2$ (0.1 mmol, 0.0430 g) were used to synthesize complex **3**. Color: red-brown. Yield: 0.852 g, 80%. M.pt.: 89 °C. Anal. Calcd. for $C_{59}H_{44}P_2N_4O_3RuS_2$: C, 65.36; H, 4.09; N, 5.17; S, 5.91%. Found: C, 64.93; H, 3.68; N, 4.83; S, 5.51%. FTIR (ATR, ν cm^{-1}): 3048 (N−H$_{hydrazide}$), 1934 (C≡O), 1734 (C═O), 1517 (C═N), 1261 (C−O), 693 (Ru−P). UV−vis (DMSO, λ_{max} nm): 553, 426, 396, 331. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): −11.20 (t, 1H, Ru−H), 16.19 (s 1H, N−H$_{hydrazide}$), 8.93−8.92 (t, 2H, J = 7.08 Hz, Ar H), 8.65 (d, 4H, J = 8.28 Hz, Ar H), 8.24 (d, 1H, J = 8.52 Hz, Ar H), 8.11 (d,1H, J = 6.36 Hz, Ar H), 8.03 (d, 1H, J = 7.96 Hz, Ar H), 7.94 (d, 1H, J = 7.56 Hz, Ar H), 7.78−7.82 (t, 1H, J = 4.01 Hz, Ar H), 7.64−7.69 (m, 6H, Ar H), 7.54−7.57 (m, 12H, Ar H), 6.93 (d, 12H, Ar H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 195.40 (Ru−C≡O), 171.69 (C═O$_{hydrazide}$), 162.97 (C−O−Ru), 149.68 (C═N−Ru), 134.97 (Ar C), 133.41 (Ar C), 132. 06 (Ar C), 130.82 (Ar C), 130.21 (Ar C), 129.75 (Ar C), 129.34 (Ar C), 128.99 (Ar C), 128.65 (Ar C), 128.24 (Ar C), 128.05 (Ar C), 127.82 (Ar C), 127.51 (Ar C). MS (ESI, m/z): calculated 1084.16, found 1085.14 [M + H]$^+$. Slow evaporation of complex in 3:1 CHCl$_3$−EtOH solvent mixture yielded needle-shaped X-ray quality crystals of complex **3**.

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*[Ru(CO)(AsPh$_3$)$_2$(L$_2$)] (**4**).* [RuHCl(CO)(AsPh$_3$)$_3$] (0.1 mmol, 0.1054 g) and **L**$_2$ (0.1 mmol, 0.0430 g) were used to synthesize complex **4**. Color: red-brown. Yield: 0.811 g, 76%. M.pt.: 92 °C. Anal. Calcd. for $C_{59}H_{42}As_2N_4O_3RuS_2$: C, 60.57; H, 3.62; N, 4.79; S, 5.48%. Found: C, 60.08; H, 3.42; N, 4.32; S, 4.99%. FT IR (ATR, ν cm^{-1}): 1932 (C≡O), 1664 (C═O), 1512 (C═N), 1264 (C−O), 692 (Ru−As). UV−vis (DMSO, λ_{max} nm): 551, 391, 330. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 8.89 (d, 2H, *J* = 7.10 Hz, Ar H), 8.44 (d, 2H, *J* = 6.72 Hz, Ar H), 8.02 (d, 2H, *J* = 8.16 Hz, Ar H), 7.90 (d, 1H, *J* = 8 Hz, Ar H), 7.86−7.83 (m, 6H, Ar H), 7.73 (d, 1H, *J* = 6.20 Hz, Ar H), 7.59 (d, 1H, *J* = 7.44 Hz, Ar H), 7.51−7.48 (t, 1H, *J* = 4.58 Hz, Ar H), 7.24−7.17 (t, 1H, *J* = 6.98 Hz, Ar H), 7.15−7.10 (m, 12H, Ar H), 6.99−6.91(m, 12H, Ar H) 7.06−7.00 (t, 1H, *J* = 7.40 Hz, Ar H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 207.15 (C≡O−Ru), 166.62 (C═O$_{hydrazide}$), 162.33 (C−O−Ru), 149.61 (C═N−Ru), 143.02 (Ar C), 137.12 (Ar C), 136.60 (Ar C), 136.31 (Ar C), 134.64 (Ar C), 133.30 (Ar C), 133.03 (Ar C), 132.63 (Ar C), 132.46 (Ar C), 131.72 (Ar C), 131.46 (Ar−C), 130.88 (Ar C), 130. 45 (Ar−C), 129.99 (Ar C), 129.36 (Ar C), 128.98 (Ar C), 128.87 (Ar C), 128.78 (Ar C), 127.65 (Ar C), 127.20 (Ar C), 127.08 (Ar C). MS (ESI, *m*/*z*): calculated 1171.05, found 1171.02 [M]$^+$. Slow evaporation of complex in 3:1 CHCl$_3$−CH$_3$CN solvent mixture yielded needle-shaped X-ray quality crystals of complex **4**.

*[Ru(H)(CO)(PPh$_3$)$_2$(L$_3$)] (**5**).* [RuHCl(CO)(PPh$_3$)$_3$] (0.1 mmol, 0.0954 g) and **L**$_3$ (0.1 mmol, 0.0421 g) were used to synthesize complex **5**. Color: red-brown. Yield: 0.825 g, 77%. M.pt.: 89 °C. Anal. Calcd. for $C_{61}H_{46}P_2N_6O_3Ru$: C, 68.21; H, 4.32; N, 7.82%. Found: C, 67.95; H, 3.87; N, 7.61%. FTIR (ATR, ν cm^{-1}): 3054 (N−H$_{hydrazide}$), 1944 (C≡O), 1707 (C═O), 1569 (C═N), 1265 (C−O), 693 (Ru−P). UV−vis (DMSO, λ_{max} nm): 497, 324. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): −13.00 (t, 1H, Ru−H), 16.23 (s, N−H$_{hydrazide}$, 1H), 8.89 (d, 4H, *J* = 6.08 Hz, Ar H), 8.72 (d, 2H, *J* = 8.60 Hz, Ar H), 8.65 (d, 2H, *J* = 6.76 Hz, Ar H), 8.56 (d, 2H, *J* = 6.00 Hz, Ar H),8.34 (d, 4H, *J* = 7.16 Hz, Ar H), 8.10−8.06 (t, 2H, *J* = 8.60 Hz, Ar H), 7.88−7.86 (m, 6H, Ar H), 7.71−7.63 (m, 12H, Ar H), 7.60−7.53 (m, 12H, Ar H).^{13}C NMR (100 MHz, CDCl$_3$, ppm): 207.97 (C≡O−Ru), 173.37 (C═O$_{hydrazide}$), 163.95 (C−O−Ru), 149.01 (C═N−Ru), 141.85 (Ar C), 140.41 (Ar C), 136.47 (Ar C), 136.35 (Ar C), 134.76 (Ar C), 133.52 (Ar C), 133.44 (Ar C), 133.09 (Ar C), 132.37 (Ar−C), 131.92 (Ar C), 130.44 (Ar C), 130.31 (Ar C), 130.08 (Ar C), 129.34 (Ar C), 129.23 (Ar−C), 128.95 (Ar C), 128.84 (Ar C), 128.72 (Ar C), 128.55 (Ar C), 128.48 (Ar C), 128.29 (Ar−C), 127.58 (Ar C), 127.48 (Ar C), 127.30 (Ar C). MS (ESI, *m*/*z*): calculated 1074.10, found 1074.22 [M]$^+$.

*[Ru(H)(CO)(AsPh$_3$)$_2$(L$_3$)] (**6**).* [RuHCl(CO)(AsPh$_3$)$_3$] (0.1 mmol, 0.1054 g) and **L**$_3$ (0.1 mmol, 0.0421 g) were used to synthesize complex **6**. Color: red-brown. Yield: 0.796 g, 72%. M.pt.: 90 °C. Anal. Calcd. for $C_{61}H_{46}As_2N_6O_3Ru$: C, 63.05; H, 3.99; N, 7.23%. Found: C, 62.72; H, 3.45; N, 6.82%. FTIR (ATR, ν cm^{-1}): 3052 (N−H$_{hydrazide}$), 1938 (C≡O), 1709 (C═O), 1536 (C═N), 1297 (C−O), 693 (Ru−As). UV−vis (DMSO, λ_{max} nm): 540, 400, 327. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): −13.84 (t, 1H, Ru−H), 16.17 (s, N−H$_{hydrazide}$, 1H), 8.89 (d, 2H, *J* = 6.60 Hz, Ar H), 8.78 (d, 2H, *J* = 5.02 Hz, Ar H), 8.26 (d, 2H, *J* = 8.16 Hz, Ar H), 8.12 (d, 2H, *J* = 6.92 Hz, ArH), 7.72 (d, 2H, *J* = 7.52 Hz, Ar H),7.60−7.56 (d, 2H, *J* = 7.01 Hz, Ar H),7.52 (d, 2H, *J* = 7.04 Hz, Ar H), 7.46−7.41 (m, 6H, Ar H), 7.17−7.09 (m, 12H, Ar H), 6.96−6.87 (d, 12H, *J* = 8 Hz, Ar H).^{13}C NMR (100 MHz, CDCl$_3$, ppm): 201.80 (C≡O−Ru), 169.68 (C═O$_{hydrazide}$), 160.03 (C−O−Ru), 150.94 (C═N−Ru),137.09 (Ar C),136.79 (Ar C), 136.53 (Ar C), 136.53 (Ar C), 133. 82 (Ar C), 133.53 (Ar C), 133.17 (Ar C), 132.59 (Ar C), 131.96 (Ar C), 131.69 (Ar C), 130.53 (Ar C), 130.12(Ar C), 130.06 (Ar C), 129.29 (Ar C), 129.01 (Ar C), 128.86 (Ar C), 128.75 (Ar C), 127.60 (Ar C), 127.30 (Ar C), 126.80 (Ar C), 126.69 (Ar C), 126.45 (Ar C). MS (ESI,*m*/*z*): calculated 1161.99, found 1161.99 [M]$^+$.

General Procedure for the N-Alkylation of Aromatic Amines with Alcohols. In a 25 mL RB flask, 5 mmol of benzyl alcohol, 5 mmol of substituted amine, 5 mol % of KOH, and 5 mL of toluene were added to a ruthenium(II) catalyst (0.5 mol %), and the reaction was carried out for 12 h at 110 °C. The content was cooled to room temperature after completion (as determined by TLC), H$_2$O (3 mL) was added, and the product was separated by extraction using ethyl acetate (3−10 mL). The crude sample was purified using *n*-hexane/ethyl acetate (7:3, v/v) mobile phase in column chromatography. ^{1}H and ^{13}C NMR spectroscopy was used to check conversions.

General Procedure for the α-Alkylation of Aromatic Ketones with Alcohols. To a solution of the Ru(II) catalyst (0.5 mol %) and KOH (5 mol %) in toluene (3 mL) was added the corresponding ketone (1 mmol) followed by the corresponding alcohol (1 mmol). The content was stirred under reflux at 110 °C for a period of 12 h. At the end, the reaction mixture was cooled, and 3 mL H$_2$O was added and extracted with 10 mL of CH$_2$Cl$_2$. The combined organic layers were dried with anhydrous Na$_2$SO$_4$. To obtain a pure product, the crude was subjected to silica gel column chromatography with an appropriate combination of petroleum ether/ethyl acetate (8:2, v/v) mobile phase. The formation of products was confirmed by ^{1}H and ^{13}C NMR spectroscopy.

General Procedure for the β-Alkylation of Secondary Alcohols with Primary Alcohols. Secondary alcohol (2.5 mmol), primary alcohol (2.5 mmol), catalyst (0.5 mol %), and KOH (5 mol %) were suspended in toluene (5 mL) using a 25 mL RB flask. The content was heated under reflux for 12 h at 110 °C. At the end, the mixture was kept at room temperature diluted with CH$_2$Cl$_2$/*n*-hexane mixture and filtered. The filtrate was concentrated, and the residue was purified using column chromatography (ethyl acetate/*n*-hexane, 2:8 (v/v) mobile phase) to provide the intended product, which was then evaluated using NMR spectroscopy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03200.

Characterization data and figures illustrating ESI-MS and NMR spectra (PDF)

Accession Codes

CCDC 2086813, 2103005, 2086814, and 2086865 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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