# Synthesis, characterization and reactivity of arene ruthenium compounds based on 2,2′-dipyridylamine and di-2-pyridylbenzylamine and their applications in catalytic hydrogen transfer of ketones

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## ABSTRACT

The synthesis and characterization of cationic arene ruthenium compounds $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}(\kappa^2\text{-dpa})]\text{BF}_4$ (**1**), $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\kappa^2\text{-dpa})]\text{BF}_4$ (**2**), $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{-RuCl}(\kappa^2\text{-dpb})]\text{BF}_4$ (**3**), $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}(\kappa^2\text{-dpb})]\text{PF}_6\text{.CH}_3\text{OH}$ (**4**) and $[(\eta^6\text{-C}_6\text{H}_6)\text{-RuCl}(\kappa^2\text{-dpb})]\text{PF}_6$ (**5**) (arene = $\text{C}_6\text{H}_6$ or $p\text{-}^i\text{PrC}_6\text{H}_4\text{Me}$; dpa = 2,2′-dipyridylamine and dpb = di-2-pyridylbenzylamine) have been described. Reactions of the representative compounds **1** and **3** with $\text{NaN}_3$, NaCN, and $\text{NH}_4\text{SCN}$ afforded substitution products $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{-Ru}(\kappa^2\text{-dpa})(\text{N}_3)]\text{BF}_4$ (**6**), $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\kappa^2\text{-dpa})(\text{CN})]\text{BF}_4$ (**7**), $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{-Ru}(\kappa^2\text{-dpa})(\text{NCS})]\text{BF}_4$ (**8**), $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\kappa^2\text{-dpb})(\text{N}_3)]\text{BF}_4$ (**9**), $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{-Ru}(\kappa^2\text{-dpb})(\text{CN})]\text{BF}_4$ (**10**) and $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\kappa^2\text{-dpb})(\text{NCS})]\text{BF}_4$ (**11**). The compounds under investigation have been characterized by elemental analyses, spectroscopic and electrochemical studies. Molecular structures of **1**, **3**, **4** and **5** have been determined crystallographically. The compounds **1**–**3** and **5** exhibited moderate catalytic activity in the reduction of ketones into corresponding alcohol in absence of a base.

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## 1. Introduction

The coordination chemistry of dipyridylamine (dpa) and its derivatives has now been the subject of a number of studies, reflecting its coordination versatility and affinity for a range of metal ions [1]. 2,2′-Dipyridylamine, which is very similar to 2,2′-bipyridine has been widely employed in the synthesis of numerous mono and polynuclear metal complexes [2]. In general, dpa behaves as a bidentate chelating ligand in mononuclear complexes bonded through both the terminal pyridine nitrogen donor sites. However, depending upon requirements about the metal centre, it also interacts in an unusual monodentate binding mode, selectively *via* one of the terminal pyridine nitrogens [3]. A number of poly-dentate ligands containing dipyridylamine as the fragment of extended ligand system have also been developed and employed in the studies ranging from metal coordination and supramolecular chemistry to synthesis of new luminescent materials [4,5]. It is well established that upon coordination with the metal centres pyridyl rings of dpa adapt either nearly co-planar or inclined pyridyl ring planes. This peculiar property of dpa and its derivatives induces either electronically or stereochemically in the systems and have been observed in a number of metal complexes [6–9]. Further, the amine proton of dpa becomes more acidic upon complexation to the metal centre and both protonated as well as deprotonated (dpa⁻) complexes based on a number of metal ions have been studied [10–12]. Loss of this proton is believed to result in planar ligand configuration in the complexes [13]. Palladium (II) and platinum (II) complexes of both the dpa and its extended deriva-tives have also been investigated as potential anticancer agents due to their structural similarity to *cis*-platin [14–16].

Furthermore, chloro-bridged dimeric arene ruthenium complexes $[\{(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}\}_2]$ (arene = $\text{C}_6\text{H}_6$, $p\text{-}^i\text{PrC}_6\text{H}_4\text{Me}$,) plays a vital role in organometallic chemistry [17]. While reactivity of these valuable precursors with a variety of ligands has been reported, its reactivity with 2,2′-dipyridylamine (dpa) and di-2-pyridylbenzylamine (dpb) have not been explored. With an objective of expanding the chemistry of dpa/dpb and to develop hydrogen transfer catalysts containing both the $(\eta^6\text{-arene})$Ru-moieties and dpa/dpb, we have synthesized and characterized a series of cationic ruthenium(II) compounds. In this paper we

present the syntheses, spectral and structural characterization of some *piano-stool* ruthenium(II) compounds containing dpa and dpb as a co-ligands. Also, we describe herein catalytic applications of **1**–**3** and **5** in reduction of acetophenone or benzophenone to corresponding alcohol under basic conditions.

## 2. Result and discussion

### 2.1. Syntheses and characterization

The synthesis of cationic mononuclear arene ruthenium compounds of the general formulations $[(\eta^6\text{-arene})RuCl_2(L)]^+$ (where L = dpa, and arene = $p$-$^i$PrC$_6$H$_4$Me, **1**; C$_6$H$_6$, **2**; L = dpb, arene = $p$-$^i$PrC$_6$H$_4$Me, **3**; arene = $p$-$^i$PrC$_6$H$_4$Me, **4** isolated as PF$_6^-$; C$_6$H$_6$, **5**) have been achieved by the reactions of chloro-bridged dimeric complexes $[\{(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl\}_2]$ (arene = C$_6$H$_6$ or $p$-$^i$PrC$_6$H$_4$Me) with 2,2′-dipyridyl-amine (dpa) and di-2-pyridylbenzylamine (dpb) in methanol under refluxing conditions. The compounds **1**–**3** and **5** have been isolated as tetrafluoroborate salts in good yields, while **4** as its hexafluorophosphate salt. The representative compounds $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})RuCl(\kappa^2\text{-dpa})]BF_4$ **1** and $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{-RuCl}(\kappa^2\text{-dpb})]BF_4$ **3**, reacted with N$_3^-$, CN$^-$ and SCN$^-$ in methanol to afford the compounds $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})Ru(\kappa^2\text{-dpa})(N_3)]BF_4$ **6**, $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})Ru(\kappa^2\text{-dpa})(CN)]BF_4$ **7**, $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})Ru(\kappa^2\text{-dpa})(NCS)]BF_4$ **8**, $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})Ru(\kappa^2\text{-dpb})(N_3)]BF_4$ **9**, $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})Ru(\kappa^2\text{-dpb})(CN)]BF_4$ **10**, and $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})Ru(\kappa^2\text{-dpb})(NCS)]BF_4$ **11**, wherein labile Cl$^-$ group from the respective precursor compounds has been replaced by N$_3^-$, CN$^-$ or SCN$^-$. A simple scheme showing the synthesis of **1**–**11** is depicted in Scheme 1.

The compounds under investigation are air-stable solids, soluble in polar organic solvents such as chloroform, methanol, ethanol, dichloromethane, acetonitrile, dimethylformamide, dimethylsulfoxide and insoluble in diethyl ether, benzene and hexane. The compounds have been characterized by elemental analyses, IR, $^1$H NMR, electronic spectral and electrochemical studies. All the compounds gave satisfactory elemental analyses (recorded in Section 4) and supported the proposed formulations.

The presence of bands associated with $\nu$(C=N), $\nu$(C=C), $\nu$(CN$^-$), $\nu$(N$_3^-$) and $\nu$(SCN$^-$) asymmetric stretching vibrations in the IR spectra of respective compounds at ∼1595–1625, 1433–1455, 2227–2248, 2022–2043, 2100–2122 cm$^{-1}$, respectively suggested the linkage of dpa, dpb CN$^-$, N$_3^-$ and SCN$^-$ [18,19]. The C=C and C=N stretching vibrations of ligands appeared at ∼1500–1600 cm$^{-1}$. In general, these bands exhibited a shift towards higher frequencies after coordination to metal centre in comparison to the uncoordinated ligands. Further, IR spectra of the compounds displayed two well separated strong and sharp bands assignable to C–N stretching vibrations associated with coordinated dipyridylamine at ∼1251 and ∼1231, ∼1025 and ∼996 cm$^{-1}$, respectively.

The $^1$H NMR spectral data of compounds summarized in experimental section displayed resonances associated with pyridyl and $\eta^6$-arene ring protons. The position and integrated intensity of various resonances corroborated well to a system involving coordination of respective ligands to the metal centre ruthenium. The assignments are based on splitting patterns and chemical shifts and comparison with the spectra of other $d^6$ tris(bipyridine) compounds [20]. In the spectra of uncoordinated ligand and the compounds containing dpa, resonances corresponding to acidic amine proton were displayed as a well resolved signal at $\delta$ 4.00 and ∼$\delta$ 11.00 ppm, respectively with respect to aromatic protons. The loss of resonances associated with acidic amine proton of free ligand in the compounds containing dpb is therefore, a strong support in favour of proposed stoichiometry of the deprotonated products. The –CH$_2$ protons resonated at $\delta$ 5.55–5.29 (s, 2H, –CH$_2$) ppm in the spectra of compounds **3**–**5** and **9**–**11**. Protons corresponding to the coordinated $p$-$^i$PrC$_6$H$_4$Me (**1**, **3**–**4**, **6**–**11**) and C$_6$H$_6$ (**2** and **5**), resonated at $\delta$ 1.10 {d, 6H, CH(CH$_3$)$_2$}, 2.24 (s, 3H, C–CH$_3$), 2.40 {m, 1H,CH(CH$_3$)$_2$}, 5.30 (dd, 4H, C$_6$H$_4$), and 5.68 (s, 6H, C$_6$H$_6$) ppm, respectively. One can see that the signals associated with arene protons exhibited an insignificant shift. Substitution of the Cl$^-$ by various monodentate ligands from precursor compounds **1** and **3** causes deshielding of various signals associated with dpa or dpb and arene protons. It may be attributed to a change in the electron density on metal centre resulting from the linkage of displacing ligands.

Electronic absorption spectra of **1**–**10** were acquired in acetonitrile ($10^{-4}$ M) at room temperature. Resulting data is summarized in experimental section and comparative spectra of **1**–**10** are depicted in Fig. S1. The metal centre ruthenium in these compounds have low spin $d^6$ configuration that provides filled $t_{2g}$ metal orbitals of proper symmetry to interact with relatively low lying unoccupied $\pi^*$ orbitals of the ligands dpa or dpb. Ruthenium(II) compounds containing dipyridylamine usually exhibit intense peaks in the UV region corresponding to ligand based $\pi$–$\pi^*$ transitions with overlapping metal-to-ligand (MLCT) transitions in the visible region [21]. The compounds under investigation are expected to give a band corresponding to metal to ligand charge transfer (MLCT) transition ($t_{1g} \rightarrow \pi^*$), whose position depends on the metal ion and ligand acting as a $\pi$-acceptor. On the basis of its intensity and position, the lowest energy transitions in visible region at ∼488–434 and 388–338 nm have been tentatively assigned to M$_{d\pi \rightarrow L^*}$ metal to ligand charge transfer transitions (MLCT). Bands in the high-energy side at ∼289–240 nm have been assigned to intra-ligand $\pi \rightarrow \pi^*$/ $n \rightarrow \pi^*$ transitions [21,22]. Absorption bands at ∼251, 257 and 249 nm, respectively in the spectra of **1**–**10** have been assigned to $\pi \rightarrow \pi^*$ transitions of the aromatic imine ligands [22].

Electrochemical properties of **1**–**3** and **5** have been followed by cyclic voltammetry in acetonitrile using 0.1 M tertabutylamm
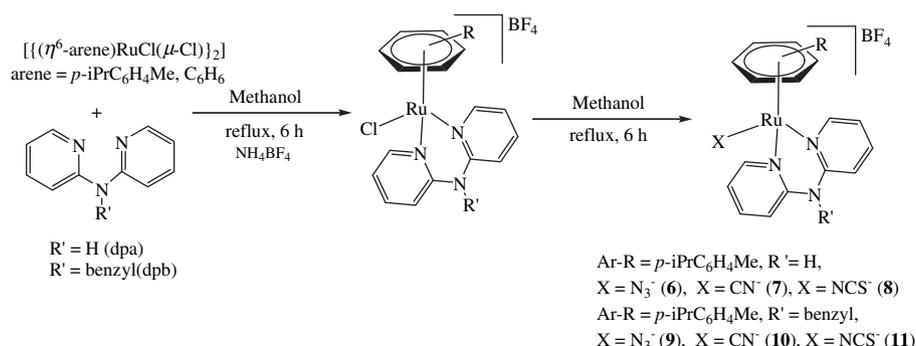


**Scheme 1.**

**Table 1**
Electrochemical data for ruthenium arene compounds 1, 2, 3, and 5 in acetonitrile solution at (rt), scan rate 100 mV/s

| Compound | $E_{1/2}$ (V) | $E_{1/2}$ (V) |
|---|---|---|
| | Ru II/III | Ligand centred |
| 1 | 0.82[a] | −1.13, −1.37, −1.99 |
| 2 | 0.74[a] | −1.78, −1.34, −1.89 |
| 3 | 0.79[a] | −1.70, −1.38, −1.97 |
| 5 | 0.72[a] | −1.24, −1.36, −1.93 |

[a] Irreversible peak.

onium perchlorate (TBAP) as supporting electrolyte. Potential of the Fc/Fc+ couple under experimental conditions was 0.10 V (80 mv) vs Ag/Ag+. Resulting data is summarized in Table 1 and selected voltammograms are depicted in Fig. S2 (supporting information). In the anodic potential window (0 to + 2.00 vs. Ag/Ag+) the compounds 1–3 and 5 exhibited only one irreversible oxidation wave at +0.82, +0.74, +0.79, and +0.72 V, respectively. These may be attributed to metal centred Ru(II/III) oxidations. One can see that the oxidation of ruthenium in benzene containing compounds takes place at lower potential in comparison to those based on p-cymene. It may be attributed to the positive inductive effect of methyl and isopropyl groups on p-cymene ring, which favors the oxidation of ruthenium at higher potential. The presence of one oxidation peak at almost the same potential in these compounds may be attributed to similar arrangement of various groups and very close electronic environments about the metal cantres. On the other hand, in cathodic potential window (0 to −2 vs. Ag/Ag+) both the dpa and dpb containing compounds exhibited three ligand based reductions (−1.13, −1.37, −1.99 V, 1; −1.34, −1.78, −1.89 V, 2; −1.38, 1.70, −1.97 V, 3; and −1.24, −1.36, −1.93 V, 5).
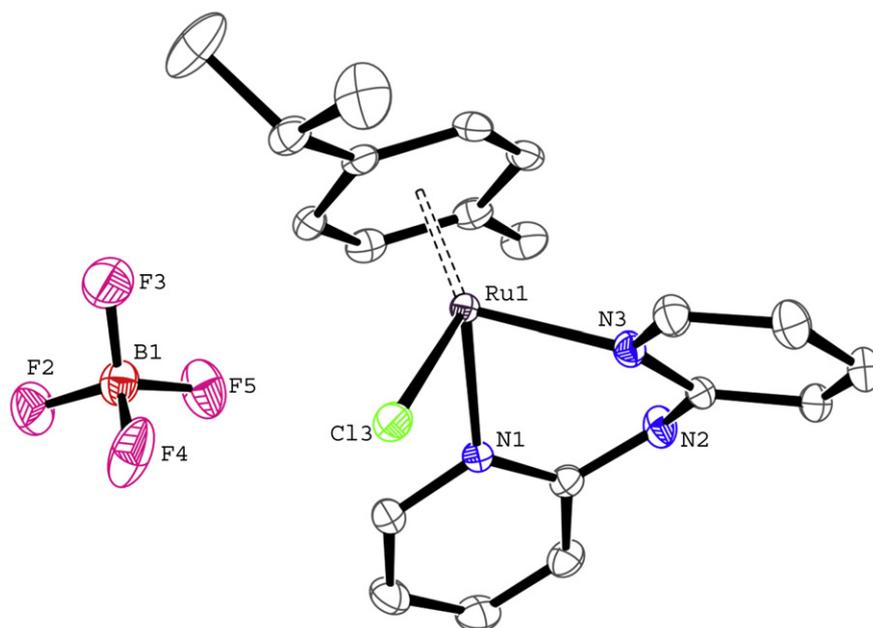
## 2.2. Molecular structures

The molecular structures of **1**, **3**, **4** and **5** have been determined by single crystal X-ray diffraction analyses. ORTEP views at 30% thermal ellipsoid probability with atom numbering scheme are shown in Figs. 1–4. Details about the data collection, solution and refinement are summarized in the experimental section and important geometrical parameters are given below the Figs. 1–4.

Compounds **1**, **3** and **4** crystallize in monoclinic system with $P2_1$, $P2_1$ and $P2_1$/c space groups. The metal centres in these iso-structral compounds exhibited typical piano-stool geometry, which is completed by hydrocarbon ligands p-$^i$PrC$_6$H$_4$Me (coordinated in $\eta^6$-mode), the chloro group and nitrogen donors from the ligand dpa and dpb. The N-N donor ligands dpa and dpb are coordinated to the metal centre in a bidentate chelating $\kappa^2$-manner through both the nitrogen atoms forming a six membered ring with the bite angles of 83.2(8) (**1**), 81.5(2) (**3**), and 81.8(13)° (**4**), respectively. The average Ru-C distances in **1**, **3** and **4** are 2.199, 2.189 and 2.198 Å. The Ru to centroid of the p-cymene ring distances are almost equal and are 1.684 (**1**), 1.689 (**3**) and 1.686 Å (**4**), respectively. The N−Ru−N and N−Ru−Cl angles are less than 90° [83.2(8), 81.5(2), and 81.8 (13)°] and are consistent with "piano stool" arrangement of various groups about the metal centre. The Ru−N bond lengths in **1**, **3** and **4** are normal and consistent with $\kappa^2$-coordination of dpa/dpb. (Ru1−N1 and Ru1−N3; Ru1−N1 and Ru1−N2; Ru1−N1 and Ru1−N2 are 2.102(19) and 2.106(19) Å, **1**; 2.101(6) and 2.105(6) Å **3**; 2.102(3) and 2.100(3) Å **4**). The M−Cl bond distances in **1**, **3** and **4** are 2.395(7), 2.401(19) and 2.404(11) Å, respectively. The Ru−N, Ru−C and Ru−Cl bond distances and various angles support "piano stool" geometry about the metal centre and are close to the one reported in other closely related compounds [23].

Compound **5** which is iso-structural with **1**, **3** and **4** crystallizes in orthorhombic crystal system with $Pca2_1$ space groups. In the asymmetric unit of **5**, there are two independent molecules which are essentially identical. Overall arrangement of various groups about the ruthenium centre in this compound also, adapted piano-stool geometry which is completed by hydrocarbon ligand C$_6$H$_6$ (bonded in $\eta^6$-manner), the chloro group and two nitrogen donors from dpb. In this compound ligand dpb is coordinated to the metal centre in bidentate manner forming a six membered ring with the bite angles of 82.4(5) and 82.9(6)°. Average Ru−C distances in the two independent molecules are 2.176 and 2.190 Å and centroids of the benzene rings are separated from Ru by 1.674 and 1.686 Å, respectively. The Ru−N distances are normal and are comparable with the distances in other ruthenium compounds containing heterocyclic



**Fig. 1.** Molecular structure and selected bond lengths (Å) and angles (°) of 1: Ru1−N1 2.102(19), Ru1−N3 2.106(13), Ru1−Cl3 2.395 (7), Ru1−C$_{av}$(arene) 2.199(2), Cg−Ru1 1.684, N1−Ru1−N3 83.27(8), N1−Ru1−Cl3 85.77(6), N3−Ru1−Cl3 87.01(6), Cl3−Ru1−Cg 128.48, N1−Ru1−Cg 128.44, N3−Ru1−Cg 128.50.
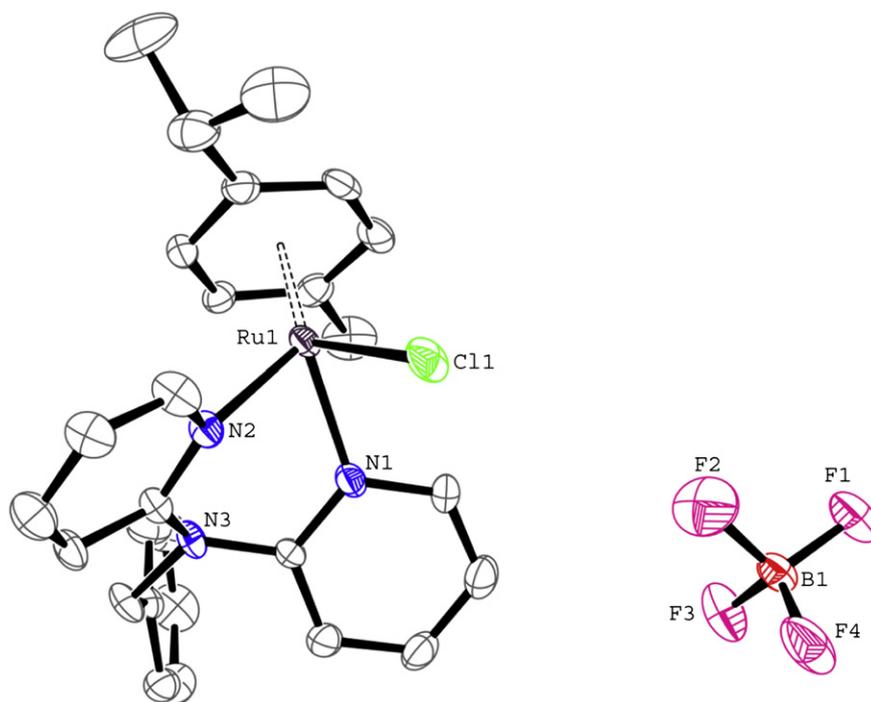
**Fig. 2.** Molecular structure and selected bond lengths (Å) and angles (°) of 3: Ru1−N1 2.105(6), Ru1−N2 2.101(6), Ru1−Cl1 2.408(9), Ru1−C$_{av}$(arene) 2.189(7), Cg Ru1 1.689, N1−Ru1−N2 81.50(2), N1−Ru1-Cl1 85.59(16), N2−Ru1−Cl1 85.96(17), Cl1−Ru1−Cg 128.09, N1−Ru1−Cg 129.44, N2−Ru1−Cg 128.44.

ligands. The M−Cl bond distances are 2.403(3) and 2.409(3) Å, respectively and are consistent with the reported values [23].
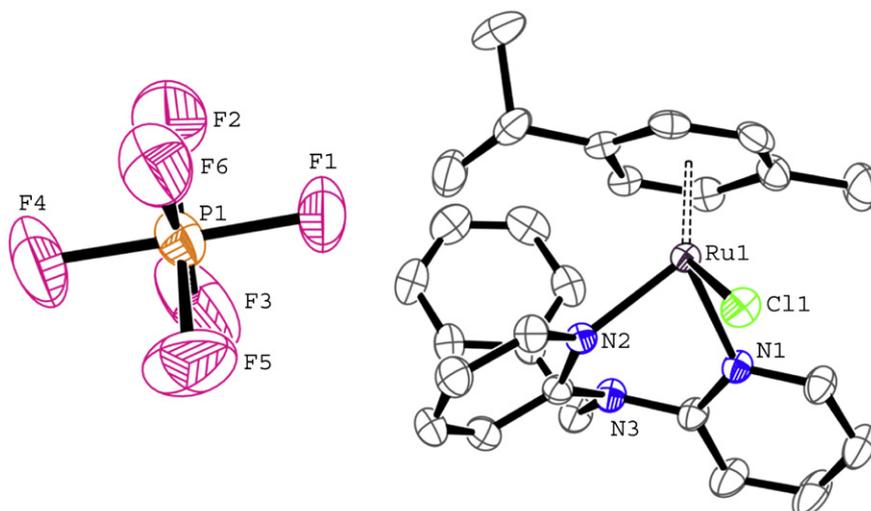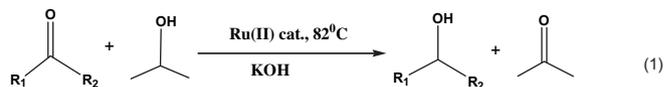
Crystal structures of **1**, **3**, **4**, and **5** revealed the presence of extensive intra- and inter-molecular C−H⋯F interactions leading to supramolecular architectures [23,24]. In compound **1**, counter ion BF$_4^-$ is encapsulated in the self-assembled cavity generated by weak interactions (Fig. S3). Some interesting motifs resulting from C−H⋯π interactions in **1**, **3**, **4**, and **5** are depicted in Figs. S4 and S5.

### 2.3. Catalytic behavior of compounds 1–3, and 5

Encouraged by applications of half-sandwich arene ruthenium compounds in transfer hydrogenation catalysis [25], we have examined the catalytic activity of **1**−**3** and **5** towards reduction of carbonyl group of ketones (Table 2).

Reduction of acetophenone or benzophenone to 1-phenyl-ethanol or 1,1-diphenylmethanol by 2-propanol was chosen as the model reaction to test the catalytic activity of arene Ru(II) N−N

$$\text{R}_1\text{C(O)R}_2 + \text{(CH}_3)_2\text{CHOH} \xrightarrow[\text{KOH}]{\text{Ru(II) cat., 82}^0\text{C}} \text{R}_1\text{CH(OH)R}_2 + \text{(CH}_3)_2\text{CO} \qquad (1)$$



**Fig. 3.** Molecular structure and selected bond lengths (Å) and angles (°) of 4: Ru1−N12.102(3), Ru1−N2 2.100(3), Ru1−Cl1 2.404 (11), Ru1−C$_{av}$(arene) 2.198(4), Cg Ru1 1.686, N1−Ru1−N2 81.85(13), N1−Ru1−Cl1 86.41(9), N2−Ru1−Cl1 86.99(9), Cl1−Ru1−Cg 126.98, N1−Ru1−Cg 129.14, N2−Ru1−Cg 129.89.
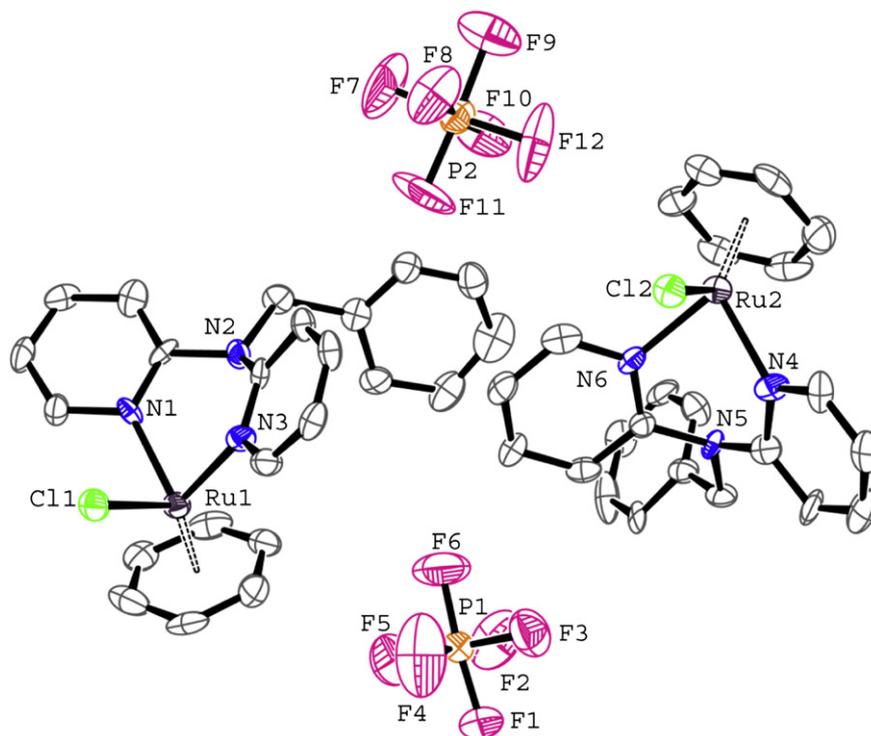
**Fig. 4.** Molecular structure and selected bond lengths (Å) and angles (°) of 5: Ru1−N12.038(15), Ru2−N4 2.093(15) Ru1−N3 2.069(14), Ru2−N6 2.067(14), Ru1−Cl1 2.409(4), Ru2−Cl2 2.403(3), Ru1−C$_{av}$(arene) 2.176(14), Ru2−C$_{av}$(arene) 2.190(16), Cg−Ru1 1.674, Cg−Ru2 1.686, N1−Ru1−N2 82.40(5), N4−Ru2−N6 82.90(6), N1−Ru1−Cl1 85.30(4), N4−Ru2−Cl2 85.0(3), N3−Ru1−Cl1 84.50(3), N6−Ru2−Cl2 85.20(3), Cl1−Ru1−Cg 128.09, Cl2−Ru2−Cg 127.79, N1−Ru1−Cg 129.02, N4−Ru2−Cg 129.36, N3−Ru1−Cg 129.03, N6−Ru2−Cg 129.43.

compounds (Eq. (1)). The reaction products were analysed by ^{1}H NMR spectroscopy and conditions employed are summarized in the experimental section. The reactions with or without addition of KOH were explored for all the isolated halide precursors. The activities of these compounds towards hydrogenation of ketones were found to be moderate. Better results obtained for acetophenone in comparison to benzophenone however, the differences were not marked. It suggested that the size of substituents on ketone is of little importance. In presence of a base like KOH, the p-cymene compounds containing dipyridylamine and its derivatives displayed higher activity than those based on benzene. The highest activity levels were found with the compounds 1 and 3 (Table 2). The activities of compounds have been explained on the basis of electron releasing groups present on aromatic ring and electronic effects about the

metal centre. It has been observed that the presence of electron releasing groups on the aromatic ring increases electron density on metal centre and the rate of transfer hydrogenation.

It is remarkable that these compounds are active in hydrogenation process in the absence of a base. The addition of a base is usually necessary in transfer hydrogenations [26] except, if a hydride which is usually unstable, is used as the starting material [27] or some sort of activation of the precursor is previously necessary [28]. In the present study, best results were achieved with 1 and 3 suggesting that the p-cymene compounds are more active in the absence of a base. Although, a tentative mechanism for these reactions have been proposed here, a prior step involving formation of the hydrides was thought to be

**Table 2**
Hydrogen transfer reactions of the compounds 1, 2, 3 and 5.

| Entry | Catalyst benzophenone | With base | | Without base | |
|---|---|---|---|---|---|
| | | Yield[a] (%) | TON[b] | Yield[a] (%) | TON[b] |
| 1 | 1 | 96 | 480 | 30 | 150 |
| 2 | 2 | 84 | 420 | 25 | 125 |
| 3 | 3 | 99 | 495 | 58 | 290 |
| 4 | 5 | 90 | 450 | 42 | 210 |
| | Acetophenone | | | | |
| 5 | 1 | 98 | 490 | 87 | 435 |
| 6 | 2 | 90 | 450 | 61 | 305 |
| 7 | 3 | 100 | 500 | 42 | 210 |
| 8 | 5 | 94 | 470 | 37 | 185 |

Reaction condition: in isopropanol with 2% catalyst w/w at 82 °C.
Yields and TON of the hydrogen transfer reactions of the compounds **1**, **2**, **3** and **5** with benzophenone and acetophenone (reaction conditions are given in experimental Section 4.2.12).
   [a] Isolated yield.
   [b] TON, turnover number = no. of moles of product/no. of moles of catalyst per unit time.
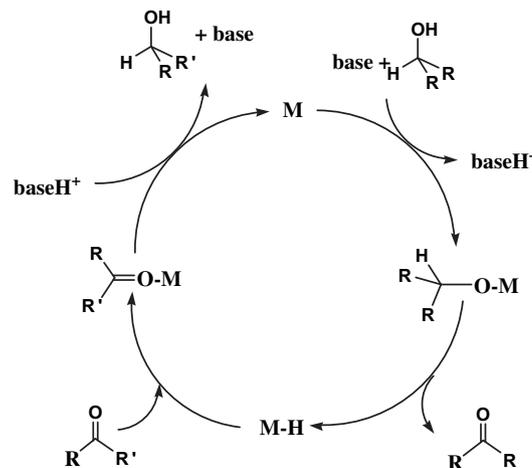


**Scheme 2.** Monohydride inner sphere mechanism for hydrogen transfer from a secondary alcohol to a ketone (M represents a transition metal compounds).

necessary. It is reasonable that these hydrides can be formulated as $[Ru(arene)H(L)]^+$. The partial de-coordination of N-donor ligand is also necessary to allow coordination of the ketone. On the basis of behavior of **1**–**5** in solution and their synthesis as depicted in Scheme 1, an inner sphere mechanism [29] has been proposed for transfer hydrogenation (TH) of ketones catalysed by chelated $\eta^n$-compounds. Compounds interact with 2-propanol in presence of KOH to form $Ru(II)–OCHR_2$ (**A**), which in turn results in the formation of $Ru–H$ (**B**) intermediate with the release of ketone. Coordination of a ketone with **B** results in the formation of an alcohol (scheme 2). Formation of the compounds containing $Ru–H$ from $Ru–Cl$ precursors are well-documented, [30] such as *in situ* generated $Ru–H$ species can act as the active catalysts for TH of ketones [30–32].

## 3. Conclusions

Through this work we have demonstrated that the ligands 2,2′-dipyridylamine (dpa) and di-2-pyridylbenzylamine (dpb) reacted with arene ruthenium compounds to afford a series of mononuclear compounds in good yields. The reactivity of resulting compounds have been examined with various bases to afford substitution products $[(\eta^6\text{-arene})Ru(dpa)X]^+$, and $[(\eta^6\text{-arene})Ru(dpb)X]^+$ (X = $N_3^-$, CN⁻ and SCN⁻). Chelation of the ligands dpa and dpb through nitrogen donor sites has been authenticated crystallographically. Furthee, it has been shown that the compounds **1**–**3** and **5** moderately catalyze reduction of ketones to corresponding alcohol and serve as an effective hydrogenating catalyst even in absence of a base.

## 4. Experimental

### 4.1. Reagents and general methods

All the synthetic manipulations were performed under aerobic conditions. The solvents were rigorously purified by standard procedures prior to their use [33]. Hydrated ruthenium(III) chloride, α-phellandrene, 2,2′-dipyridylamine (dpa) (all Sigma−Aldrich) were used as received without further purifications. The precursor complexes, $[\{(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl\}_2]$ [34] (arene = $C_6H_6$, and $p\text{-}^iPrC_6H_4Me$) and the ligand di-2-pyridylbenzylamine (dpb) [35] were prepared and purified following the literature procedures. Elemental analyses for C, H and N were performed on an Exeter Analytical Inc. Model CE-440 Elemental Analyzer. IR and electronic absorption spectra were recorded on a Varian 3300 FT-IR and Shimadzu UV-1700 series spectrophotometers, respectively. $^1H$ NMR spectra were obtained on a JEOL AL 300 FT-NMR spectrometer at room temperature using DMSO-$d_6$ as a solvent. Residual protonated species in the deuterated solvents were used as internal references; all the $^1H$ shifts (s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad) are reported relative to the external TMS. Cyclic voltammetric measurements were performed on a CHI 620c Electrochemical Analyzer. Platinum working electrode, platinum wire auxiliary electrode, and Ag/Ag⁺ reference electrode were used in a standard three-electrode configuration. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte and solution concentration was ca. $10^{-3}$.

### 4.2. Syntheses

#### 4.2.1. Synthesis of $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)RuCl(\kappa^2\text{-}dpa)]BF_4$ (**1**)

To a suspension of $[\{(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-Cl})Cl\}_2]$ (0.612 g, 1.0 mmol) in methanol (25 ml), dpa (0.171 g, 1.0 mmol) was added and the contents of flask were heated under reflux for 8 h. After cooling to room temperature orange solution thus obtained was concentrated to dryness under reduced pressure. It afforded

compound **1** as an orange solid which was recrystallized from $CH_2Cl_2$-petroleum ether (40−60 °C). Yield: 0.528 g, 86%. Microanalytical data: $C_{20}H_{23}ClN_3RuBF_4$ [Mr = 528.7 g/mole] requires: C, 45.52; H, 4.20; N, 7.96%. Found: C, 45.50; H, 4.18; N, 7.98%. $^1H$ NMR ($\delta$ ppm): 1.28 (d, 12H, CH(CH$_3$)$_2$), 1.84 (s, 6H, CH$_3$), 2.82 {m, 2H, CH(CH$_3$)$_2$}, 5.69 {m, 4H, $\eta^6\text{-}p\text{-}^iPrC_6H_4Me$ (C$_6$H$_4$)}, 6.01 {m, 4H, $\eta^6\text{-}p\text{-}^iPrC_6H_4Me$ (C$_6$H$_4$)}, 11.6 (s, 1H. NH), 8.11 (t, 2H), 7.60 (t, 2H), 7.26 (t, 2H), 7.10 (d, 2H). IR (KBr pellet, cm$^{-1}$): 3400 (s), 1626 (s), 1577 (s), 1470 (s), 1424 (s), 1396 (m), 1317 (w), 1251 (s), 1228 (s), 1144 (m), 1075 (w), 1028 (s), 1003 (w), 995 (s), 915 (w), 878 (w), 790 (s), 773 (s), 698 (s), 528 (m), $\nu$(BF$_4$) 1056. UV−vis. (CH$_3$CN, $\lambda_{max}$ nm, $\epsilon$): 457 (890), 338 (15080), 273 (38410), 249 (38910).

#### 4.2.2. Synthesis of $[(\eta^6\text{-}C_6H_6)RuCl(\kappa^2\text{-}dpa)]BF_4$ (**2**)

Compound **2** was prepared using $[\{(\eta^6\text{-}C_6H_6)Ru(\mu\text{-Cl})Cl\}_2]$ (0.500 g, 1.0 mmol) in place of $[\{(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-Cl})Cl\}_2]$, following the above procedure for **1**. It isolated as a yellow microcrystalline solid. Yield: 0.472 g, 94%. Microanalytical data: $C_{16}H_{15}ClN_3RuBF_4$ [Mr = 472.64 g/mole] requires: C, 40.66; H, 3.20; N, 8.89. Found: C, 40.62; H, 3.24; N, 8.86%. $^1H$ NMR ($\delta$ ppm): 5.68 (s, 6H, C$_6$H$_6$), 10.4 (s, 1H), 8.10 (t, 2H), 7.64 (t, 2H), 7.36 (t, 2H), 7.15 (d, 2H). IR (KBr pellets, cm$^{-1}$): 3432 (s), 1595 (s), 1520 (w), 1469 (s), 1433 (s), 1394 (m), 1255 (s), 1230 (s) 1184 (m), 1136 (m), 1079 (m), 1028 (s), 994 (m) 844 (s), 758 (s), 698 (s), $\nu$(BF$_4$) 1056. UV−vis. (CH$_3$CN, $\lambda_{max}$ nm, $\epsilon$): 485 (1980), 375 (15400), 285 (38070), 245 (38570).

#### 4.2.3. Synthesis of $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)RuCl(\kappa^2\text{-}dpb)]BF_4$ (**3**)

To a suspension of $[\{(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-Cl})Cl\}_2]$ (0.612 g, 1.0 mmol) in methanol (25 ml), dpb (0.261 g, 1.0 mmol) was added and the contents of flask were heated under reflux overnight. Resulting reaction mixture was filtered to remove any solid impurities. A saturated solution of ammonium tetrafluroborate dissolved in 5 ml methanol was added to the filtrate and left for slow crystallization in a refrigerator. Slowly, yellow microcrystalline product separated which was filtered, washed with diethyl ether and dried *in vaccuo*. Yield: 0.512 g, 83%. Microanalytical data: $C_{27}H_{29}BClF_4N_3Ru$ [Mr = 618.87 g/mol] requires: C, 52.40; H, 4.72; N, 6.79%. Found: C, 52.42; H, 4.70; N, 6.80%. $^1H$ NMR ($\delta$ ppm): 1.30 {d, 12H, CH(CH$_3$)$_2$}, 1.86 (s, 6H, CH$_3$), 2.80 {m, 2H, CH(CH$_3$)$_2$}, 5.64 {m, 4H, $\eta^6\text{-}p\text{-}^iPrC_6H_4Me$ (C$_6$H$_4$)}, 6.11 {m, 4H, $\eta^6\text{-}p\text{-}^iPrC_6H_4Me$ (C$_6$H$_4$)}, 8.24 (d, 2H), 7.95 (t, 2H), 7.86 (s, 2H), 7.45 (d, 2H), 7.23 (d, 2H), 7.06 (d, 3H), 5.41 (s, 2H). (KBr pellets, cm$^{-1}$): 3083 (w), 3037 (w), 1599 (s), 1487 (s), 1459 (s), 1445 (s), 1345 (m), 1265 (m), 1228 (m), 1144 (m), 1053 (w), 1029 (s), 1003 (w), 988 (s), 915 (w), 878 (w), 790 (s), 773 (s), 698 (s), 528 (m), 502 (w), 448 (w), 435 (w). UV−vis. (CH$_3$CN, $\lambda_{max}$ nm, $\epsilon$): 452 (1480), 352 (4870), 290 (38240), 242 (39240).

#### 4.2.4. Synthesis of $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)RuCl(\kappa^2\text{-}dpb)]PF_6.MeOH$ (**4**)

It was prepared following exactly the same procedure for **3**, except that ammonium hexafluorophosphate was used in place of ammonium tetrafluroborate. Yield: 0.492 g, 80%. Microanalytical data: $C_{28}H_{33}PClOF_6N_3Ru$ [Mr = 709.08 g/mol] requires: C, 47.43; H, 4.69; N, 5.93%. Found: C, 47.40; H, 4.70; N, 5.91%.

#### 4.2.5. Synthesis of $[(\eta^6\text{-}C_6H_6)RuCl(\kappa^2\text{-}dpb)]PF_6$ (**5**)

Compound **4** was prepared using $[\{(\eta^6\text{-}C_6H_6)Ru(\mu\text{-Cl})Cl\}_2]$ (0.500 g, 1.0 mmol) in place of $[\{(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-Cl})Cl\}_2]$ following the above procedure for **3**. Yield: 0.432 g, 86%. Microanalytical data: $C_{23}H_{21}ClF_6N_3PRu$ [Mr = 620.93 g/mole] requires: C, 44.49; H, 3.41; N, 6.77%. Found: C, 44.52; H, 3.39; N, 6.78%. $^1H$ NMR ($\delta$ ppm): 5.64 (s, 6H, C$_6$H$_6$), 8.10 (d, 2H), 7.64 (t, 2H), 7.36 (t, 2H), 7.15 (d, 2H), 7.23 (d, 2H), 7.06 (d, 3H), 5.43 (s, 2H). IR (KBr pellets, cm$^{-1}$): 3085 (w), 3040 (w), 1610 (s), 1577 (s), 1487 (s), 1444 (s), 1427 (s), 1345 (m), 1255 (s), 1230 (m), 1146 (m), 1030 (w), 1003 (w), 989 (w),

878 (w), 790 (s), 773 (s), 698 (s), 528 (m), 502 (w), 440 (w), 436 (w), $\nu(PF_6^-)$ 840. UV–vis. (CH$_3$CN, $\lambda_{max}$ nm, $\epsilon$): 473 (1030), 342 (9220), 283 (22130), 257 (38750).

### 4.2.6. Synthesis of [($\eta^6$-p-$^i$PrC$_6$H$_4$Me)Ru($\kappa^2$-dpa)(N$_3$)]BF$_4$ (6)

To a methanolic suspension of 1 (0.1 g, 0.18 mmol), NaN$_3$ (0.012 g, 0.18 mmol) was added and refluxed for 4 h, whereupon yellow solution turned pale yellow in color. The solvent was rotatory evaporated and yellow solid thus obtained was dissolved in CH$_2$Cl$_2$ and filtered. The filtrate was concentrated to 2 ml and hexane was added to induce precipitation. Light yellow product separated which was washed with diethyl ether and dried under vacuum. Yield: 0.078 g, 78%. Microanalytical data: C$_{20}$H$_{23}$N$_6$RuBF$_4$ [Mr = 534.31 g/mole] requires C, 44.96; H, 4.15; N, 15.73. Found: C, 44.98; H, 4.12; N, 15.70%. $^1$H NMR ($\delta$ ppm): 1.34 {d, 12H, CH(CH$_3$)$_2$}, 1.81 (s, 6H, CH$_3$), 2.84 {m, 2H, CH(CH$_3$)$_2$}, 5.70 {m, 4H, $\eta^6$-p-$^i$PrC$_6$H$_4$Me (C$_6$H$_4$)}, 6.10 {m, 4H, $\eta^6$-p-$^i$PrC$_6$H$_4$Me (C$_6$H$_4$)}, 12.1 (s, 1H), 8.10 (t, 2H), 7.64 (t, 2H), 7.24 (t, 2H), 7.11 (d, 2H). (KBr pellets, cm$^{-1}$): 3424 (s), 2022 (s), 1620 (s), 1575 (s), 1477 (s), 1426 (s), 1390 (m), 1316 (w), 1264 (m), 1228 (m), 1145 (m), 1065 (w), 1000 (w), 992 (s), 912 (w), 876 (w), 791 (s), 776 (s), 699 (s), 527 (m), $\nu$(BF$_4$) 1055. UV–vis. (CH$_3$CN, $\lambda_{max}$ nm, $\epsilon$): 455 (1310), 360 (11630), 288 (22276), 240 (29580).

The compounds 7–8 were synthesized following exactly the same procedure as adopted for 6. Characterization data of these compounds are given below.

### 4.2.7. Characterization data of [($\eta^6$-p-$^i$PrC$_6$H$_4$Me)Ru($\kappa^2$-dpa)(CN)]BF$_4$ (7)

Yield: 0.098 g, 98%. Microanalytical data: C$_{21}$H$_{23}$N$_4$RuBF$_4$ [Mr = 519.31 g/mole] requires C, 48.57; H, 4.46; N, 10.79. Found: C, 48.55; H, 4.44; N, 10.80%. $^1$H NMR ($\delta$ ppm): 1.33 {d, 12H, CH(CH$_3$)$_2$}, 1.77 (s, 6H, CH$_3$), 2.80 {m, 2H, CH(CH$_3$)$_2$}, 5.71 {m, 4H, p-$^i$PrC6H4Me (C$_6$H$_4$)}, 6.14 {m, 4H, p-$^i$PrC6H4Me (C$_6$H$_4$)}, 10.1 (s, 1H), 8.24 (t, 2H), 7.54 (t, 2H), 7.34 (t, 2H), 7.10 (d, 2H). IR (KBr pellet, cm$^{-1}$): 3424 (s), 2227 (s), 1625 (s), 1577 (s), 1474 (s), 1430 (s), 1394 (m), 1320 (w), 1255 (m), 1232 (m), 1145 (m), 1065 (w), 1020 (w), 996 (s), 922 (w), 877 (w), 792 (s), 774 (s), 690 (s), 526 (m), $\nu$(BF$_4$) 1055. UV–vis. (CH$_3$CN, $\lambda_{max}$ nm, $\epsilon$): 458 (1542), 355 (10632), 286 (20276), 251 (36810).

### 4.2.8. Characterization data of [($\eta^6$-p-$^i$PrC$_6$H$_4$Me)Ru($\kappa^2$-dpa)(SCN)]BF$_4$ (8)

Yield: 0.082 g, 82%. Microanalytical data: C$_{21}$H$_{23}$N$_4$SRuBF$_4$ [Mr = 551.37 g/mole] requires C, 45.75; H, 4.20; N, 10.16. Found: C, 45.73; H, 4.22; N, 10.14%. $^1$H NMR ($\delta$ ppm): 1.31 {d, 12H, CH(CH$_3$)$_2$}, 1.77 (s, 6H, CH$_3$), 2.80 {m, 2H, CH(CH$_3$)$_2$}, 5.71 {m, 4H, $\eta^6$-p-$^i$PrC$_6$H$_4$Me (C$_6$H$_4$)}, 6.14 {m, 4H, $\eta^6$-p-$^i$PrC$_6$H$_4$Me (C$_6$H$_4$)}, 11.1 (s, 1H), 8.26 (t, 2H), 7.52 (t, 2H), 7.32 (t, 2H), 7.11 (d, 2H). IR (cm$^{-1}$, KBr pellet): 3411 (s), 2100 (s), 1610 (s), 1587 (s), 1477 (s), 1428 (s), 1388 (m), 1322 (w), 1261 (m), 1228 (m), 1142 (m), 1065 (w), 1022 (w), 998 (s), 920 (w), 876 (w), 790 (s), 773 (s), 692 (s), 526 (m), $\nu$(BF$_4$) 1055. UV–vis. (CH$_3$CN, $\lambda_{max}$ nm, $\epsilon$): 460 (1742), 345 (9945), 283 (19276), 253 (32843).

### 4.2.9. Synthesis of [($\eta^6$-p-$^i$PrC$_6$H$_4$Me)Ru($\kappa^2$-dpb)(N$_3$)]BF$_4$ (9)

Compound 9 was prepared using 3 (0.1 g, 0.16 mmol) and NaN$_3$ (0.011 g, 0.16 mmol) following the method for 6. Yield: 0.082 g, 82%. Microanalytical data: C$_{27}$H$_{29}$BF$_4$N$_6$Ru [Mr = 625.44 g/mole] requires: C, 51.85; H, 4.67; N, 13.44. Found: C, 51.86; H, 4.70; N, 13.46%. $^1$H NMR ($\delta$ ppm): 1.28 {d, 12H, CH(CH$_3$)$_2$}, 1.84 (s, 6H, CH$_3$), 2.82 {m, 2H, CH(CH$_3$)$_2$}, 5.60 {m, 4H, $\eta^6$-p-$^i$PrC$_6$H$_4$Me (C$_6$H$_4$)}, 6.10 {m, 4H, $\eta^6$-p-$^i$PrC$_6$H$_4$Me (C$_6$H$_4$)}, 8.69 (d, 2H), 7.77 (t, 2H), 7.86 (s, 2H), 7.37 (d, 2H), 7.26 (d, 2H), 7.08 (d, 3H), 5.55 (s, 2H). IR (KBr pellets, cm$^{-1}$): 3088 (w), 3043 (w), 2037 (s), 1598 (s), 1540 (s), 1477 (s), 1445 (s), 1346 (m), 1255 (m), 1230 (m), 1146 (m), 1080 (w), 1020 (w), 985 (s), 918 (w), 876 (w), 792 (s), 772 (s), 696 (s), 528 (m), 502 (w), 448 (w), 438 (w) $\nu$(BF$_4$) 1056. UV–vis. (CH$_3$CN, $\lambda_{max}$ nm, $\epsilon$): 439 (1722), 347 (1850), 309 (10430), 268 (22130).

The compounds 10–11 were synthesized following exactly the same procedure as adopted for 9. Characterization data of the compounds is summarized below.

### 4.2.10. Characterization data of [($\eta^6$-p-$^i$PrC$_6$H$_4$Me)Ru($\kappa^2$-dpb)(CN)]BF$_4$ (10)

Yield: 0.097 g, 97%. Microanalytical data: C$_{28}$H$_{29}$BF$_4$N$_4$Ru [Mr = 609.44 g/mole] requires: C, 55.18; H, 4.80; N, 9.19%. Found: C, 55.20; H, 4.82; N, 9.20%. $^1$H NMR ($\delta$ ppm): 1.26 {d, 12H, CH(CH$_3$)$_2$}, 1.79 (s, 6H, CH$_3$), 2.86 {m, 2H, CH(CH$_3$)$_2$}, 5.40 {m, 4H, $\eta^6$-p-$^i$PrC$_6$H$_4$Me (C$_6$H$_4$)}, 6.12 {m, 4H, $\eta^6$-p-$^i$PrC$_6$H$_4$Me (C$_6$H$_4$)}, 8.70 (d, 2H) 7.88 (t, 2H), 7.41 (s, 2H), 7.33 (d, 2H), 7.25 (d, 2H), 7.11 (d, 3H), 5.48 (s, 2H). IR (KBr pellets, cm$^{-1}$): 3083 (w), 3037 (w), 2237 (s), 1618 (s), 1568 (s), 1544 (s), 1488 (s), 1436 (s), 1336 (m), 1245 (m), 1226 (m), 1136 (m), 1086 (w), 1026 (w), 993 (s), 919 (w), 874 (w), 794 (s), 774 (s), 694 (s), 525 (m), 504 (w), 445 (w), 436(w), $\nu$(BF$_4$) 1045 cm$^{-1}$. UV–vis. (CH$_3$CN, $\lambda_{max}$ nm, $\epsilon$): 454 (1378), 345 (8639), 253 (29560).

### 4.2.11. Characterization data of [($\eta^6$-p-$^i$PrC$_6$H$_4$Me)Ru($\kappa^2$-dpb) (NCS)]BF$_4$ (11)

Yield: 0.076 g, 76%. Microanalytical data: C$_{28}$H$_{29}$BF$_4$SN$_4$Ru [Mr = 641.50 g/mole] requires: C, 52.43; H, 4.56; N, 8.73%. Found: C, 52.41; H, 4.58; N, 8.74%. $^1$H NMR ($\delta$ ppm): 1.27 {d, 12H, CH(CH$_3$)$_2$}, 1.78 (s, 6H, CH$_3$), 2.89 {m, 2H, CH(CH$_3$)$_2$}, 5.42 {m, 4H, $\eta^6$-p-$^i$PrC$_6$H$_4$Me (C$_6$H$_4$)}, 6.10 {m, 4H, $\eta^6$-p-$^i$PrC$_6$H$_4$Me (C$_6$H$_4$)}, 8.70 (d, 2H), 7.88 (t, 2H), 7.41 (s, 2H), 7.33 (d, 2H), 7.25 (d, 2H), 7.11 (d, 3H), 5.45 (s, 2H). IR (KBr pellets, cm$^{-1}$): 3076 (w), 3026 (w), 2118 (s), 1608 (s), 1576 (s), 1542 (s), 1465 (s), 1433 (s), 1330 (m), 1240 (m), 1224 (m), 1138 (m), 1088 (w), 1027 (w), 996 (s), 914 (w), 877 (w), 788 (s), 764 (s), 692 (s), 521 (m), 501 (w), 442 (w), 433 (w), $\nu$(BF$_4$) 1056. UV–vis. (CH$_3$CN, $\lambda_{max}$ nm, $\epsilon$): 442 (1456), 355 (4872), 248 (26734).

### 4.2.12. General procedure for the catalytic studies

Hydrogen transfer experiments for hydrogenation of acetophenone or benzophenone were carried out using 2-propanol as the solvent and hydrogen source at the refluxing temperature of solvent (82 °C). Each run was repeated thrice to ensure reproducibility. Following general procedure was employed: A solution of ketone (1 mmol), KOH (0.2 ml of a 0.2 M solution in 2-propanol) and corresponding catalyst (0.002 mmol) was heated under reflux in 10 ml of 2-propanol for 24 h. 2-Propanol was removed under vaccum and an aliquot of remaining product was analysed by $^1$H NMR in CDCl$_3$. The yield of the process was calculated considering the relative integrals of ketone and alcohol.

### 4.2.13. X-ray structure determinations

Suitable crystals for single crystal X-ray diffraction analyses for 1, 3, 4 and 5 were obtained from CH$_2$Cl$_2$/petroleum ether (40–60 °C) at room temperature by slow diffusion method. Preliminary data on the space group and unit cell dimensions as well as intensity data were collected on Rigaku-RAXIS RAPID II diffractometer using graphite-monochromatized Mo-K$\alpha$ ($\lambda$ = 0.71073 Å) radiation. Structures were solved by direct methods (SHELXS 97) and refined by full-matrix least squares on $F^2$ (SHELX 97) [36]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model. The computer program PLATON was used for analyzing the interaction and stacking distances [36c]. CCDC-742999 (1), 768447 (3), 768449 (4), and 768448 (5) contain supplementary crystallographic data for this paper.

Compound 1. Formula C$_{20}$H$_{23}$ClN$_3$RuBF$_4$, Mr = 528.7, Monoclinic, space group P2$_1$, $a$ = 8.8572(2) Å, $b$ = 12.9699(2) Å, $c$ = 9.5615(2) Å,

## Acknowledgements

## Appendix. Supplementary data

CCDC 742999, and 768447−768449 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.06.003.

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