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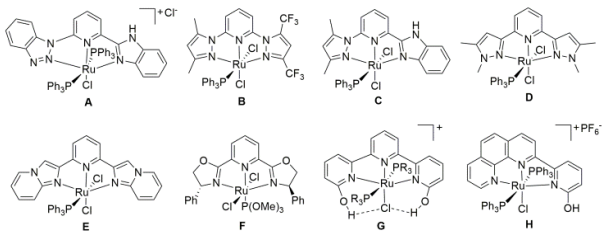
# Ruthenium(II) Complexes of 4'-(aryl)-2,2':6',2''-terpyridyl Ligands as Simple Catalysts for Transfer Hydrogenation of Ketones

Apurba Maity,[a] Amit Sil,[a] Sanjib K. Patra*[a]

**Abstract:** A series of cationic $[Ru(\mathbf{L})(PPh_3)_2Cl]^+$ (**1-3**) and neutral $[Ru(\mathbf{L})(PPh_3)Cl_2]$ (**4-6**) Ru(II) complexes have been synthesized by reacting $[RuCl_2(PPh_3)_2]$ with 4'-(aryl)-2,2':6',2''-terpyridyl based ligands (**L1-L3**) by varying the aryl groups (tolyl, phenyl and 4-fluorophenyl). The synthesized Ru(II) complexes have been unambiguously characterized by various spectroscopic tools such as FTIR and multinuclear NMR as well as HRMS analyses. The neutral complexes (**4**-**6**) have also been structurally characterized by single crystal X-ray diffraction studies. Photophysical and electrochemical studies of the Ru(II) complexes have been carried out to understand the substituent effect of the 4′-aryl group of the ligands **L1-L3**. These Ru(II) complexes show good catalytic activity in transfer hydrogenation (TH) of ketones with a wide substrates scope in refluxing isopropanol. Optimization study reveals that the neutral Ru(II) complexes act as better catalysts over cationic Ru(II) complexes for TH reactions. Finally, $[Ru(\mathbf{L1})(PPh_3)_2H]^+$ (**7**) having [Ru(II)-H] functionality has been successfully synthesized, isolated and proposed as the catalytically active species. The controlled experiment by [Ru(II)-H] complex in the absence of base has been carried out to establish the mechanism of catalytic TH of ketones.

## Introduction

Catalytic transfer hydrogenation (TH) of unsaturated organic compounds has become a reliable reduction strategy to access various hydrogenated products over other conventional methods of reduction. It is the most useful catalytic method for hydrogenation not only because it is a clean and environmentally benign process but also due to its easy manipulation, relatively low cost and wide substrate scope.[1] Use of 2-propanol as hydrogen source for TH reaction of ketones leads to an equilibrium reaction which can be shifted to the alcohol product by employing 2-propanol as solvent. One of the biggest concerns in industrial transfer hydrogenation is to replace the use of $NaBH_4$ and $LiAlH_4$ facilitating the hazardous free workup, extending the substrate scope, reducing the amount of side products and enhancing the reaction efficiency. In this regards, exploration of various types of ligands and their transition metal complexes are strongly desired for transfer hydrogenation. The development of transition metal complexes of cobalt(II),[2] nickel(II),[2a,3] iron(II),[2a,4] osmium(II),[5] rhodium(I/III)[6] and iridium(I/III)[7] as catalysts for the TH of ketones is a fast growing research field. However, ruthenium(II) complexes have been paid much more interest as these are robust and highly efficient in general.[1c,8] In the past few years, great improvements of ruthenium(II)-catalyzed TH have been witnessed in several aspects including the development of the diversity of ligands. In this area, Noyori and co-workers have developed Ru(II) complexes containing N-tosylethylenediamine or β-amino alcohol based ligands exhibiting efficient catalytic activity in the asymmetric transfer hydrogenation of ketones and imines.[9] After their pioneering work, a significant number of similar ligands and their transition metal complexes have been documented.[10] In this regard, Baratta et al. have reported a series of cyclometalated Ru(II) complexes containing 2-(aminomethyl)pyridine ligands as efficient catalysts for the transfer hydrogenation of ketones.[11] In some cases, the presence of a N-H functionality as an accelerating group offers high reactivity for TH reaction.[11g,m,o,p] Although, there are several Ru(II) catalysts featuring no acceleration functionality have also been known for the TH of ketones.[12] An extensive exploration of NNN tridentate pincer ligands based ruthenium catalysts for TH of ketones was seen over the past few years (scheme 1).[1c,13] Yu et al. synthesized several NNN pincer type ligands and its corresponding ruthenium(II) complexes for the TH of ketones with or without acceleration functionality.[14] For example, air and moisture-stable ruthenium(II) complex **A** exhibited excellent transfer hydrogenation of ketones in refluxing isopropanol due to the hemilabile unsymmetrical coordinating environment and NH functionality.[14f] Complex **B**, bearing (trifluoromethyl)-pyrazolyl functionality converted ketones to their corresponding alcohols in maximum of 99% yield.[14d] Room temperature transfer hydrogenation of ketones and aldehydes was achieved in 2-propanol by using ruthenium(II) complex **C** as catalyst under aerobic condition.[14k] Ruixiang Li and coworkers developed a




**Scheme 1.** Representative examples of recently reported NNN pincer ligands based ruthenium(II) complexes as catalysts for TH reactions

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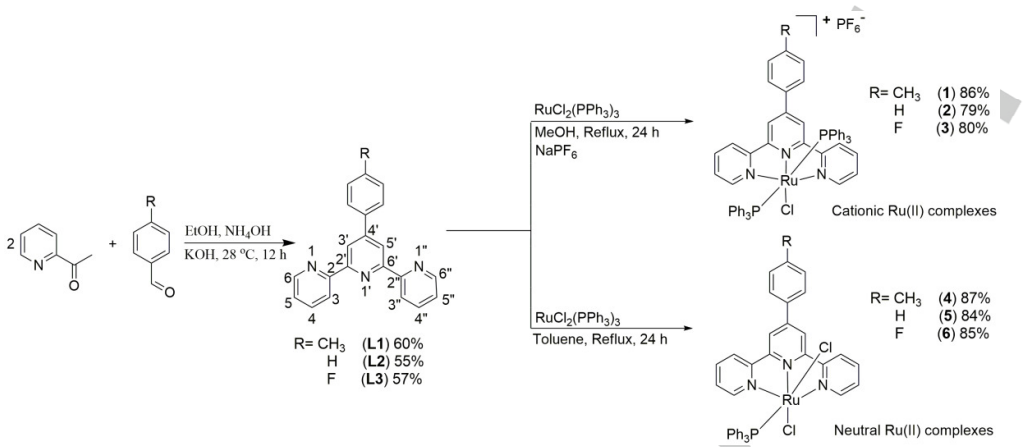
symmetrical pyridyl-2,6-pyrazolyl ligand based ruthenium(II) complex (**D)** which showed good to excellent catalytic activity in transfer hydrogenation of wide substrate of ketones.[13e] Song and coworkers also reported symmetrical Ru(II) complex (**E)** and observed almost quantitative transfer hydrogenation of ketones with wide substrate scope.[13c] Additionally, complex **E** was proved to be an improved catalyst than its corresponding cationic analogue. In another report by Pizzano and coworkers, asymmetric transfer hydrogenation of N-aryl imines derived from acetophenones was carried out by using the catalyst **F** bearing both a pybox (2,6-bis(oxazoline)pyridine) and a monodentate phosphite ligand.[13b] For the Ru(II) complex **G**, the use of 6,6′-dihydroxy terpyridine (dhtp) as a rigid bifunctional ligand provided the directing effect of proton transfer events with substrates coordinated to the metal centre.[13h] However, the catalyst was found to be highly sensitive towards bulky ketones, giving no TH product for benzophenone. Recently, Kundu and coworkers reported bifunctional Ru(II)-(phenpy-OH) [phenpy-OH: 2-(2-pyridyl-2-ol)-1,10-phenanthroline] complex **H** that catalyzed a diverse range of substrates of ketones and nitriles using 2-propanol as hydrogen source.[13a]

Design and development of versatile ligands are the key issues to attain highly active transition metal complexes as catalysts. Nitrogen-containing heterocyclic ligands and their transition metal complexes have been widely studied in coordination chemistry, homogeneous catalysis and organic synthesis.[15] Over the past few years, NNN ligands such as Pybox,[16] 2,6-bis(imino)pyridines[17] 2,6-bis-(benzimidazole-2-yl)-pyridine[15d] and 2,2':6',2''-terpyridines (tpy)[18] have been paid much more attention in coordination chemistry, homogeneous catalysis, functional materials and physical chemistry due to their tunable properties and potential applications. Easily functionalizable terpyridyl based N-donor ligands with its tunable electronic character may function as an ideal alternative of organophosphine ligands. Tpy ligand has been considered as an unusually strong *π*-acceptor relative to other N-donors and is also oxidatively and thermally robust.[18e,19] The advantageous properties of the tpy based ligands allow the chemists for exploring it in variety of catalytic processes such as asymmetric cyclopropanation,[18e,20] oxidation and dehydrogenation of alcohols,[21] co-oligomerization of alkenes,[22] allylic alkylation,[23] hydrosilylation,[24] Negishi coupling,[25] and rearrangement of oxaziridines.[26]

Although a great potential of terpyridine family has been implicated in a variety of catalytic processes, they have been exploited as ligands for the development of catalysts for the transfer hydrogenation of ketones to a limited extent.[8l,13h,27] In this work, neutral and cationic ruthenium(II) complexes of 4'-(aryl)-2,2':6',2''-terpyridine ligands have been synthesized and characterized by multinuclear NMR analyses and X-ray crystallographic studies aiming to develop simple and economical Ru(II) catalysts for transfer hydrogenation of ketones.

## Results and Discussion

**Synthesis and characterization of Ru(II) complexes:** A simple and synthetically ease 4'-(aryl)-2,2':6',2''-terpyridines (**L1-L3**) have been selected as ligands by varying the aryl group (tolyl, phenyl and 4-fluorophenyl) to tune their electronic properties. The synthesis of the ligands, **L1-L3**, was performed following Kröhnke method affording 55-60% yield respectively as shown in Scheme 2.[28] The synthesis involves condensation of *p*- tolyldehyde with two equivalent of acetylpyridine in ethanol leading to the formation of the central pyridine ring in the presence of ammonia as a base. The formation of ligands was confirmed by $^{1}H$, $^{13}C\{^{1}H\}$ NMR and mass spectrometry ($ESI^{+}$). Cationic (**1**-**3**) and neutral (**4**-**6**) ruthenium(II) complexes were synthesized by reacting an equimolar amount of ligands and $RuCl_2(PPh_3)_3$ under argon atmosphere to realize the role of electronic effect of tpy ligands as varied by different 4′-aryl groups and also the charge of complexes on catalytic process. Refluxing in methanol followed by the addition of $NaPF_6$ afforded the cationic Ru(II) complexes, **1**-**3** in 79-86% yield. Use of toluene as refluxing solvent produced neutral complexes in 84-87% yield (Scheme 2). Both the cationic and neutral ruthenium(II) complexes were found to be stable in air and moisture. Multinuclear NMR analyses of all the Ru(II) complexes are in well agreement with their expected chemical structures. The $^{1}H$ NMR signal for the terpyridyl-CH (6, 6″) protons adjacent to the pyridyl-N in free ligand **L1** appear at 8.68 ppm and that for the cationic complex **1** and neutral complex **4** are shifted downfield to 9.03 and 9.47 ppm respectively, as a result of ligand coordination to the Ru(II) centre. The similar trend in the downfield shift is also observed for the other cationic and neutral complexes. The $^{13}C\{^{1}H\}$ NMR spectra of all the ligands (**L1**-**L3**) display a signal at 136.9-137.1 ppm for the pyridyl-CH (6, 6″) adjacent to pyridyl-N. After coordination to Ru(II), the signal is shifted to 155.1-155.7 ppm. In $^{31}P\{^{1}H\}$ NMR spectra (in $CDCl_3$), signal for **4-6** appears at 41.4-41.7 ppm indicating that the environment around the $PPh_3$ ligand is identical for all the neutral complexes. For the cationic complexes (**1**-**3**) the single resonance appears at 20.0-20.2 ppm, revealing the presence of two identical $PPh_3$ ligands around Ru(II) centre. The formation of the cationic and neutral Ru(II) complexes is further confirmed by HRMS ($ESI^{+}$) and CHN analyses. For the cationic complexes **1-3**, the respective peaks (m/z) at 984.1983, 970.1848 and 988.1804 for $[M-PF_6]^{+}$ are observed, whereas for the neutral complexes (**4-6)** the characteristic signals attributed to




**Scheme 2.** Synthetic route for the cationic (**1**-**3**) and neutral (**4**-**6**) ruthenium(II) complexes.

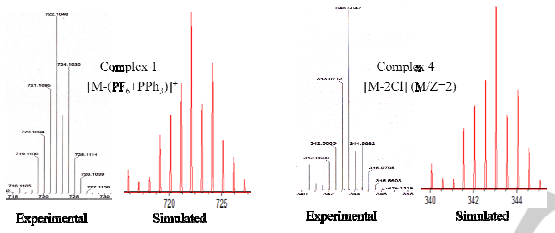



**Figure 1.** Simulated and experimental isotopic distribution pattern for the molecular ion peak.

$[M\text{-}Cl]^+$ are obtained at 721.1061, 708.0929 and 726.0850 respectively. Experimental and simulated isotopic distribution pattern for the molecular ion peak are in perfect agreement as depicted in Figure 1. The structure of the neutral complexes **4**-**6** was further confirmed by single crystal X-ray crystallographic studies (Figure 2). The six-coordinated Ru(II) center formed the distorted pseudo-octahedral environment in the solid state for all the three neutral complexes. The Ru-N distances for the central pyridine ring (N2) of complexes are shorter than for the two terminal pyridine rings (N1 & N3). The Cl1-Ru1-Cl2 angles are in the range of 87.66(6)˚-87.91(7)˚ in all the neutral Ru(II) complexes, indicating that the two chloride ligands are in the *cis* position. The $PPh_3$ ligand adopts a nearly orthogonal position with respect to the NNN plane of tpy ligand as manifested by P1-Ru1-N1, P1-Ru1-N2 and P1-Ru1-N3 bond angles which are in the range of 90.66(16)˚-93.30(17)˚, 92.20(18)˚-93.50(19)˚ and 91.56(17)˚-91.66(18)˚ (Table 1) respectively. The aryl and the terpyridyl groups are not perfectly coplanar as manifested by the corresponding torsional angles. Photophysical and electrochemical characterization of all the Ru(II) complexes (**1**-**6**) were performed to monitor the electronic effect of their substituent at 4' position. Optical properties of all the Ru(II) complexes **1**-**6** were studied in $CH_2Cl_2$ at $1\times10^{-5}$ M concentration (Figure S37 in supporting information). The cationic complexes exhibit a broad absorption band in the visible region at $\lambda_{max}$ of 490 nm with $\varepsilon_{max}$ in the order of $10^4$ $M^{-1}cm^{-1}$, attributing to the metal to ligand charge transfer (MLCT) transition. Interestingly, the neutral complexes show a significant bathochromic shift by 50-52 nm than that of the cationic Ru(II) complexes. For all the Ru(II) complexes, a second set of absorption bands in the UV region ($\lambda_{max}$ of 270-325 nm) appears which may be assigned to the spin-allowed π–π* transition involving the terpyridyl moiety.[18a,29] Cyclic voltammetry analysis of the Ru(II) complexes was carried out in $CH_2Cl_2$ using *n*-$Bu_4NPF_6$ (0.1 M) as supporting electrolyte, Pt-disc working electrode, Pt-wire counter electrode and Ag/AgCl reference electrode. All the cationic complexes **1**-**3** show one-electron

**Table 1.** Important bond distances and bond angles of neutral Ru(II) complexes **4**-**6**.

| | **4** | **5** | **6** |
|---|---|---|---|
| Bond Distances (Å) | | | |
| Ru1-N1 | 2.072(6) | 2.056(5) | 2.074(2) |
| Ru1-N2 | 1.945(6) | 1.942(5) | 1.946(6) |
| Ru1-N3 | 2.047(6) | 2.063(6) | 2.080(7) |
| Ru1-P1 | 2.293(2) | 2.289(2) | 2.314(2) |
| Ru1-Cl1 | 2.461(2) | 2.464(18) | 2.479(2) |
| Ru1-Cl2 | 2.460(2) | 2.463(17) | 2.447(2) |
| Bond Angles (˚) | | | |
| Cl1-Ru1-Cl2 | 87.69(7) | 87.66(6) | 87.91(7) |
| P1-Ru1-N1 | 92.61(19) | 90.66(16) | 93.30(17) |
| P1-Ru1-N2 | 93.50(19) | 92.41(16) | 92.20(18) |
| P1-Ru1-N3 | 91.66(18) | 93.03(16) | 91.56(17) |
| P1-Ru1-Cl1 | 179.08(7) | 176.92(6) | 178.46(8) |
| P1-Ru1-Cl2 | 93.10(8) | 94.76(6) | 92.33(7) |
| Torsional angle (˚) | | | |
| C7-C8-C16-C17 | -15.31 | 31.60 | 17.13 |
| C9-C8-C16-C21 | -12.45 | 29.96 | 18.02 |

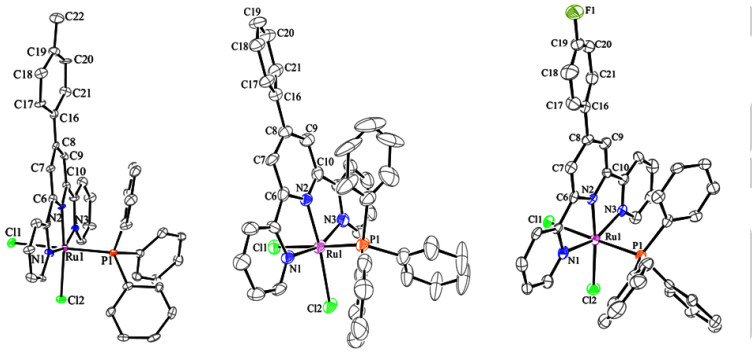



**Figure 2.** Molecular structures of neutral complexes **4**-**6** with hydrogen atom omitted for clarity. The thermal ellipsoid are drawn at 40% of probability.

reversible oxidation wave with $E_{1/2}$ value in the range of 0.94-0.96 V due to the Ru(II)/Ru(III) process as shown in Figure 3. Similar electrochemical behavior was also observed for all the neutral complexes **4**-**6** with significantly lower reduction potential with $E_{1/2}$ in 0.63-0.64V. The positive charge in the cationic complexes and the two π-acceptor $PPh_3$ ligands make the Ru(II) centers relatively electron deficient than that of the neutral complexes. Consequently, the cationic Ru(II) centers in complexes (**1**-**3**) exhibit higher reduction potential than that of neutral complexes (**4**-**6**).

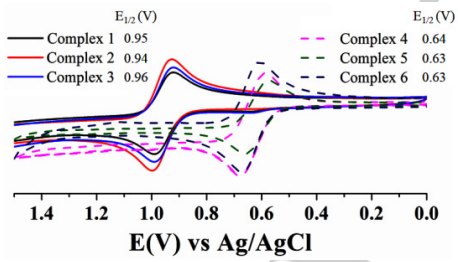



**Figure 3.** Cyclic voltammograms of Ru(II) complexes (**1**-**6**) in $CH_2Cl_2$ using $TBAPF_6$ as supporting electrolyte, Pt disc working electrode, and Ag/AgCl reference electrode. Scan rate at 100 mV/s.

**Transfer hydrogenation (TH) of ketones by the synthesized Ru(II) complexes:** In our initial studies, TH of acetophenone was chosen as the model reaction. Complexes **1** and **4** were tested as catalysts in refluxing isopropanol to screen the reaction condition. The reaction was carried out at 0.5 mol% of catalyst loading with a molar ratio of 200/20/1 for ketone/base/catalyst in the presence of NaOH as a base under an argon atmosphere. As observed from the Table 2 (entries, 1 and 4), the neutral complex **4** acts as a better catalyst than the cationic complex **1**. Presumably, the electron-rich neutral catalyst as indicated by the cyclic voltammetric studies, exhibiting lower reduction potential by 0.31-0.32 V ($E_{1/2}$) compared to the cationic ones (*vide supra*), facilitates the reduction.[7g,9i] Over the period of 2 hours, the TH reaction of acetophenone reached to 66% and 84% of isolated yield using the complexes **1** and **4** respectively. To see the effect of various substitutions at 4'-position of terpyridyl unit on the catalytic process, complexes **2**, **3**, **5** and **6** were employed as catalysts under the same reaction condition (entry 2, 3, 5 and 6 in Table 2). For both the cationic and neutral complexes, no significant alteration of reaction yields was observed, revealing the independency of functionalization of ligands on the catalytic process. In entry 7, the reaction using catalyst **4** was deliberately quenched after 1 hour where only 63% of the starting material was converted to the 1-phenylethanol. From this observation, it can be concluded that the optimum reaction time to achieve maximum yield is 2 hours. A significant decrease in yield was observed when the molar ratio of base was decreased (Table 2, entry 8). The reaction was carried out in air (Table 2, entry 9) and over the period of 4 hours, only 49% yield could be achieved, indicating that inert atmosphere is

**Table 2**. Optimization of the reaction condition for the transfer hydrogenation of acetophenone.[a]

| Entry | Cat. | base | Time, h | Yield, %[b] |
|---|---|---|---|---|
| 1 | 1 | NaOH | 2 | 66 |
| 2 | 2 | NaOH | 2 | 64 |
| 3 | 3 | NaOH | 2 | 67 |
| 4 | 4 | NaOH | 2 | 84 |
| 5 | 5 | NaOH | 2 | 81 |
| 6 | 6 | NaOH | 2 | 80 |
| 7 | 4 | NaOH | 1 | 63 |
| 8[c] | 4 | NaOH | 2 | 67 |
| 9[d] | 4 | NaOH | 4 | 49 |
| 10 | 4 | - | 4 | N.R.[e] |

[a] Reaction condition: ketone 2.0 mmol; *i*PrOH = 20 mL; ketone/base/cat. = 200/20/1; $N_2$ atmosphere; 82 °C. [b] Isolated yield. [c] Ketone/base/cat. = 200/10/1. [d] Reaction in air. [e] No reaction.

necessary to keep the catalyst active. No product was found in the absence of base (Table 2, entry 10), suggesting that presence of base is crucial to the relative success of the reaction. For comparison, the effect of various bases on the reaction in the presence of neutral ruthenium(II) catalyst **4**, NaOH, KOH, $^{t}$BuOK, $K_2CO_3$ and $NaHCO_3$ were used as the bases (Table 3). After 2 hours of reaction time, the corresponding alcohol from acetophenone was achieved with yield of 84%, 82% and 78% by using the bases NaOH, KOH and $^{t}$BuOK respectively. While using $K_2CO_3$ and $NaHCO_3$, relatively lower yield of 71% and 65% was observed under same reaction condition. So it can be concluded that strong bases like NaOH, KOH and $^{t}$BuOK act as better reaction promoter. So based on the above results, the molar ratio of 200/20/1 for ketone/base/catalyst, 0.5 mol% of neutral ruthenium(II) complex **4** as catalyst and NaOH as the base in refluxing isopropanol under a nitrogen atmosphere were chosen as the optimized reaction condition. However, KOH and $^{t}$BuOK also worked well as bases under the same reaction condition.

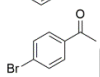
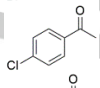
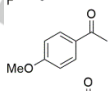
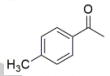
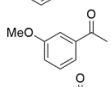
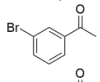
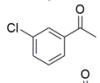
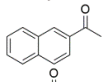
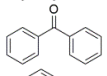
**Table 3**. Optimization of bases for the transfer hydrogenation of acetophenone catalyzed by Ru(II) complex 4.[a]

| Entry | Cat. | Base | Time, h | Yield, %[b] |
|---|---|---|---|---|
| 1 | 4 | NaOH | 2 | 84 |
| 2 | 4 | KOH | 2 | 82 |
| 3 | 4 | $^{t}$BuOK | 2 | 78 |
| 4 | 4 | $K_2CO_3$ | 2 | 71 |
| 5 | 4 | $NaHCO_3$ | 2 | 65 |

[a] Reaction condition: ketone, 2.0 mmol; *i*PrOH = 20 mL; ketone/base/cat. = 200/20/1; $N_2$ atmosphere; 82 °C. [b] Isolated yield.

This optimized reaction condition was followed to other ketones in the transfer hydrogenation to access other hydrogenated products (Table 4). For this purpose, various substituted acetophenone, aryl alkyl ketones, aliphatic cyclic ketones, α,β-unsaturated ketones and diones were assessed for transfer hydrogenation reaction in a systematic way. Reaction time for every case was optimized to achieve maximum isolated yield. The electronic effect in TH reactions is very obvious, in which acetophenone bearing electron–withdrawing substituents such as chloro, bromo and fluoro reacts efficiently in 1.5 hours (Table 4, entries 2, 3, 4) with a TON value in the range of 156-172. On the other hand, the electron-donating methyl or methoxy substituents (Table 4, entries 5, 6) make the ketone substrates more electron rich and therefore, they need longer reaction time to achieve higher yield. Figure 4 demonstrates the relationship between the electronic effect of the substrates and the reaction yield by giving the positive slope, supporting the fact that the substrates with electron withdrawing group favour the TH than the substrates with electron donating group. Notably, 2'-substituted acetophenone needed longer time to gain maximum isolated yield than their corresponding analogues bearing substituents at *meta* position (Table 4, entries 8, 9 *vs*. 11, 12) as increasing the steric hindrance around the keto group in the substrates retarded the reaction rate. Although a contradictory result was observed for 2-methoxyacetophenone achieving 77% yield over a period of 3 hours, whereas 71% isolated yield was observed for 3-methoxyactophenone after 4 hours (Table 4, entry 7 *vs* 10).

**Table 4**. Transfer hydrogenation of various ketones catalyzed by **4**.[4]

| Entry | Ketone | Time, h | Yield, %[b] | TON |
|---|---|---|---|---|
| 1 |  | 2 | 83 | 166 |
| 2 |  | 1.5 | 78 | 156 |
| 3 |  | 1.5 | 86 | 172 |
| 4 |  | 1.5 | 84 | 168 |
| 5 |  | 5 | 75 | 150 |
| 6 |  | 3 | 81 | 162 |
| 7 |  | 3 | 77 | 154 |
| 8 |  | 3 | 78 | 156 |
| 9 |  | 2.3 | 83 | 166 |
| 10 |  | 4 | 71 | 142 |
| 11 |  | 2 | 81 | 162 |
| 12 |  | 1.8 | 80 | 160 |
| 13 |  | 2.5 | 81 | 162 |
| 14 |  | 2 | 83 | 166 |
| 15 |  | 4 | 72 | 144 |
| 16 |  | 3 | 75 | 150 |
| 17 |  | 8 | 53 | 106 |
| 18 |  | 8 | 56 | 112 |

[a] Reaction condition: ketone, 2.0 mmol; *i*PrOH = 20 mL; ketone/base/cat. = 200/20/1; Argon atmosphere; 82 °C; [b] Isolated yield.

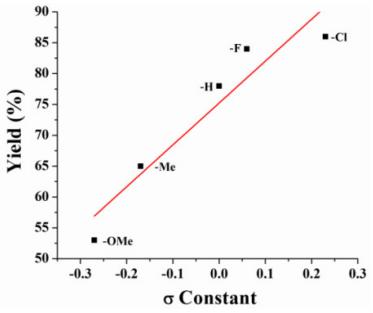
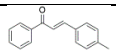
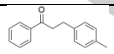
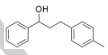
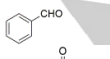
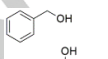
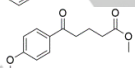
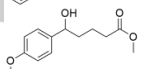
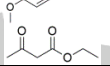
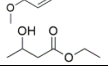



**Figure 4.** Plot demonstrating the electronic effect of the substituents at 4-position of acetophenone derivatives in transfer hydrogenation (For each of the cases, yields were obtained after 1.5 h.)

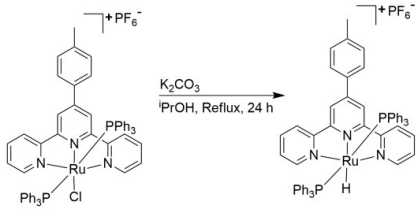
This result attributed to the fact that in comparison to the resonance effect, the inductive effect of the substituents is more effective in influencing reduction rates. Methoxy group has -I effect which is most effective when substituted at *ortho* position, resulting highest conversion of product in comparatively less time.[14f] Aryl ketones like 1-acetonaphthone and benzophenone reacted smoothly with a TON value of more than 160 to give the desired products in 81-83% yield in 2.5 and 2 hours respectively (Table 4, entry 13, 14). Heterocyclic ketones also showed good reactivity (TON 144-150 after 4 and 3 hours for entry 15 and 16 respectively) under the same reaction condition (Table 4, entry 15, 16). Transfer hydrogenation of aliphatic cyclic ketones was also carried out to obtain moderate yields after prolong reaction time (Table 4, entry 17, 18). For our curiosity and to extend the substrate scope, α,β-unsaturated ketone, 1-phenyl-3-p-tolylprop-2-en-1-one was employed as substrate for TH reaction with the Ru(II) catalyst. Over a period of 8 hours, both the alkene and keto group had undergone reduction to give a major product in 52% yield (Supporting information). A minor product resulting from the selective reduction of alkene bond over ketone group was also obtained in 21% yield (Table 5, entry 1). Benzaldehyde responded very weakly under this reaction condition (Table 5, entry 2). Transfer hydrogenation of unsymmetrical diones was also examined under the same reaction condition. Interestingly, selective reduction of the more active ketone keeping the ester group intact was observed (entry 3 and 4 in Table 5).

**Table 5**. Extended substrate scope with catalyst **4**.[a]

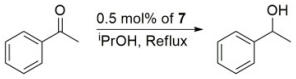
| Entry | ketones | Time, h | products | Yield, %[b] | TON |
|---|---|---|---|---|---|
| 1 |  | 8 |  | 21 | 166 |
| | | |  | 52 | |
| 2 |  | 6 |  | 34 | 68 |
| 3 |  | 4 |  | 70 | 140 |
| 4 |  | 6 |  | 43 | 86 |

[a] Reaction condition: substrate, 2.0 mmol; *i*PrOH = 20 mL; substrate/base/cat. = 200/20/1; Argon atmosphere, 82 °C; [b] Isolated yield.

**Transfer hydrogenation reaction mechanism:** Based upon the related reported literature[14d-f,30] it can be proposed that *in situ* generated [Ru-H] complexes act as catalytically active species in most of the Ru(II)-catalyzed transfer hydrogenation reactions. For this reason, isolation of catalytically active Ru(II)-H complex was attempted. While treating complex **1** with $K_2CO_3$ in refluxing 2-propanol, the corresponding dark brown colored $[Ru(\mathbf{L1})(PPh_3)_2(H)]^+$ complex (**7**) was successfully isolated in 70% yield (Scheme 3). $^1H$ NMR ($CDCl_3$) confirmed the presence of Ru(II)-H functionality by showing a characteristic triplet resonance at -6.15 ppm with J value of 24 Hz (Fig. 5a). $^{31}P$ NMR also confirmed the formation of hydride complex by showing a doublet with perfect agreement in $^2J_{P\text{-}H}$ value of two-bond P-H coupling (H-Ru(II)-$PPh_3$). The formation of the complex **7** was confirmed by HRMS analysis, showing a molecular ion peak at 950.2402 $[M\text{-}PF_6]^+$. Simulated and experimental isotopic distribution pattern for the molecular ion peak of **7** are in perfect agreement (Fig. 5b). Complex **1** was tested as catalyst under the same reaction condition as in Table 2, entry 1 without base and it was observed that complex **1** did not produce any transfer hydrogenated product of acetophenone. As anticipated, under the optimized reaction




**Scheme 3.** Isolation of the catalytically active [Ru(II)-H] species.




**Scheme 4.** Base free TH using Ru(II)–H catalyst **7**.

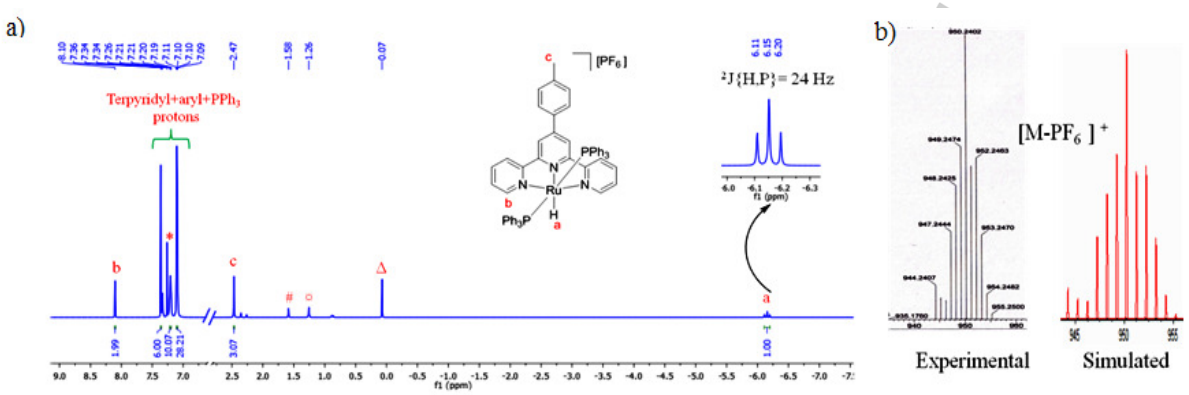
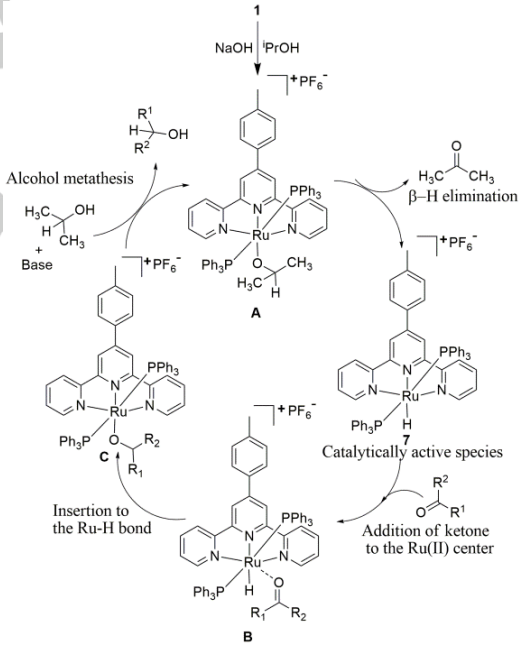



**Figure 5.** a) $^1$H NMR (600 MHz, $CDCl_3$) spectrum of **7** (* = residual $CHCl_3$, # = $H_2O$, ¤ = H grease, Δ = TMS). b) Experimental and simulated isotopic distribution for the molecular ion peak of **7** obtained from HRMS study.

condition complex **7** catalyzed the transfer hydrogenation of acetophenone in the absence of NaOH, resulting the desired product in 63% yield over a period of 18 hours (Scheme 4). However, in the presence of NaOH the precatalyst **1** furnished the TH reaction in 2 hours (Table 2, entry 1). Developing base free transfer hydrogenation protocol by transition metal catalyst is the recent trend in this area.[7g,31] In this regard, complex **7** acted as base free catalyst for the transfer hydrogenation of acetophenone. This result suggests that complex **1** acts as precatalyst for the transfer hydrogenation of acetophenone. In the presence of base it is readily converted to [Ru(II)-H] complex which is the catalytically active species.

Prompted by the above experimental result and the reported literature, a plausible mechanism involving a Ru-H intermediate as the catalytically active species is proposed as shown in scheme 5.[13a,13c,14d-f] The transfer hydrogenation mechanism utilizes 2-propanol both as solvent and hydrogen donor. For example the cationic complex **1** reacts with 2-propanol in presence of base to produce Ru(II)-alkoxide **A**, then upon β-H elimination it forms a Ru-H catalytically active intermediate **7** and release of acetone is occurred. Coordination of ketone substrates to the metal centre (**B**) and followed by the insertion to the Ru-H bond affords Ru(II)-alkoxide **C** which undergoes base-mediated alcohol metathesis to regenerate species **A** and complete the catalytic cycle, producing the desired alcohol products. Thus, an inner-sphere mechanism considering complex **1** as precatalyst is established. In the last step of the catalytic cycle, exchange of the alkoxide product with another alcohol is accelerated in the presence of base.[14g] Hence it is not surprising for observing longer reaction time to yield 1-phenylethanol in 63% yield catalyzed by complex **7** without using NaOH base. To prove, we conducted transfer hydrogenation of acetophenone by **7** as catalyst in presence of base. The reaction furnished the desired product in 68% of yield only after 2 hours (supporting information).




**Scheme 5.** Proposed mechanism of TH of ketone by the cationic Ru(II) catalyst.

## Conclusions

In conclusion, versatile archetypical tridentate (NNN) terpyridyl supported Ru(II) cationic and neutral complexes have been synthesized and characterized successfully. Functionalization at 4'-position of terpyridyl unit was varied in metal complexes to modify the electronic effect. These ruthenium complexes, featuring no acceleration functionality (such as -NH), show good catalytic activity in transfer hydrogenation (TH) of ketones with a substrate to catalyst ratio of 200:1 in refluxing isopropanol which acts as hydrogen source. Optimized reaction condition was employed to electron-rich/poor, diaryl, cycloaliphatic ketones, dione and α,β-unsaturated ketones. This substrate scope study reveals that the electron-poor ketones react at faster rate than the electron-rich ketones, whereas the *ortho* substituted aromatic ketones react slowly than the *para* substituted ones except the methoxy substituted ketones. Neutral Ru(II) complexes exhibited better catalytic activity than cationic Ru(II) complexes because of having lower reduction potential ($E_{1/2}$) by 0.30 V, facilitating reduction of ketones. Most importantly, the catalytically active species [Ru(II)-H] complex (**7**) from **1** was isolated and characterized unambiguously to understand the mechanism of transfer hydrogenation. As expected, the complex **7** can act as TH catalyst under base free condition. Further development of Ru(II) catalyst of the tailored terpyridyl ligands for more efficient TH and hydrosilylation is underway.

## Experimental Section

**General considerations.** Unless otherwise mentioned all chemicals were of analytical grade, obtained from commercial sources (Sigma aldrich, Alfa aesar, Spectrochem) and were used without further purification. Reactions for the preparation of Ru(II) complexes as well as all the catalytic reactions were conducted under an argon atmosphere by using standard Schlenk techniques. The glasswares were oven-dried (at 180 $^{o}$C) and cooled under vacuum. Solvents were purified by following the standard protocol. Substrates such as 1-phenyl-3-p-tolylprop-2-en-1-one and methyl 5-(4-methoxyphenyl)-5-oxopentanoate were synthesized as described in the literature (Supporting information). Acetyl pyridine, 4-fluorobezaldehyde, 4-methylbenzaldehydeand benzaldehyde were purchased from Spectrochem while all the substrates were obtained either from Avra or spectrochem. $RuCl_3 \cdot xH_2O$ was acquired from Arora Matthey Ltd. $PPh_3$ was purchased from Spectrochem and purified by recrystallization from absolute ethanol followed by sublimation. $Ru(PPh_3)_3Cl_2$ was synthesized following the procedure described in the literature.[32] Silica gel (60–120 mesh) used for column chromatography, was purchased from Merck. Eluting systems for column chromatography purifications were determined by thin layer chromatography (TLC) analysis. TLC plates were visualized under UV light (254 nm). Solvents were evaporated under reduced pressure using a rotary evaporator.

$^{1}$H (600 MHz, 400 MHz), $^{13}C\{^{1}H\}$ (150 MHz, 100 MHz), $^{31}P\{^{1}H\}$ (162 MHz), $^{19}F\{^{1}H\}$ (376 MHz) NMR spectra were obtained from Bruker Lambda spectrometer using $CDCl_3$ unless otherwise mentioned. Spectra were internally referenced to residual solvent peaks (δ = 7.26 ppm for proton and δ = 77.23 for carbon (middle peak) in $CDCl_3$. All coupling constants (*J*) are given in Hz. The HRMS mass spectometry was recorded in ESI$^{+}$ mode (70 eV) in Waters mass spectrometer (Model: Xevo-G2QTOF). The absorption spectra were collected using a Shimadzu (Model UV-2450) spectrophotometer. FTIR spectra were recorded in Spectrum-BX (Perkin Elmer) on KBr pallet. Cyclic voltammetric studies were performed on a BASi Epsilon electrochemical workstation in $CH_2Cl_2$ with 0.1 M *tetra*-n-butylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. The working electrode was a BASi Pt-disk electrode, the reference electrode was Ag/AgCl and the auxiliary electrode was a Pt-wire. The ferrocene/ferrocenium couple occurs at $E_{1/2}$ = +0.51(70) V versus Ag/AgCl under the same experimental conditions.

**X-ray data collections and refinement.** The dark reddish brown block shaped single crystals of complexes **4-6** suitable for X-ray crystallography, were obtained by layering hexanes on DCM solution of Ru(II) complexes. Single-crystal X-ray data was collected on a Bruker-APEX-II CCD X-ray diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2) K using graphite-monochromated Mo $K_\alpha$ radiation ($\lambda_\alpha$ = 0.71073 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software package,[33] and the data were corrected for absorption using the SADABS program.[34] Pertinent crystallographic data for complexes **4-6** is summarized in Table S3 (Supporting information). Complex **4** crystallizes in the monoclinic $P2_1/n$ whereas **5** and **6** crystallize in $P2_1/c$ space groups. Two independent molecules of complexes **5** and **6** were located in the asymmetric unit with negligible differences in their metrical parameters. CCDC 1588786-1588788 contain 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. The structures were solved by SHELXT[35] and refined with SHELXL[36] using Olex2 program.[37] The molecular structure was generated by using ORTEP-3 for Windows Version 2.02.[38] Because of the failure to identify the solvent molecules for **5**, SQUEEZE option in PLATON program was used to remove the unidentified intensities from the overall intensity data.[39] The hydrogen atoms were included in geometrically calculated positions in the final stages of the refinement and were refined according to the typical riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters.

**Synthesis and characterization**

**General procedure for the synthesis of cationic ruthenium(II) complexes.** In an oven dried Schlenk flask, a mixture of 4'(aryl)-2,2':6',2''-terpyridine (0.1 mmol), $RuCl_2(PPh_3)_3$ (0.096 g, 0.1 mmol ) and degassed MeOH (12 mL) were added and heated to reflux for 24 hrs under argon atmosphere. The reaction mixture was turned to wine red clear solution with few solid impurities. After cooling to room temperature the reaction mixture was filtered through a bed of

celite which was washed several times by dry MeOH. Then $NaPF_6$ ( 0.25 mmol) was added to the concentrated solution of the filtrate and was kept in the deep freeze for overnight to precipitate a red-brown fine crystalline solid. The solid was filtered off, washed with diethyl ether (3×10 mL) and dried under reduced pressure to furnish analytically pure compounds.

**Complex 1.** According to the general procedure for the synthesis of cationic ruthenium(II) complexes, 4'(4-methylphenyl)-2,2':6',2''-terpyridine (0.032 g, 0.1 mmol) and $RuCl_2(PPh_3)_3$ (0.096 g, 0.1 mmol ) were refluxed in degassed MeOH (12 mL) and then addition of $NaPF_6$ (0.042 g, 0.25 mmol) afforded cationic ruthenium(II) complex **1** which was washed with diethyl ether (3×10 mL) to furnish analytically pure cationic ruthenium(II) complex **1** (0.097 g) in 86% yield. $^1$H NMR ($CDCl_3$, 400 MHz): δ 2.46 (s, 3H, Me-H), 7.04-7.08 (m, 14H), 7.17-7.21 (m, 18H), 7.42 (d, 2H, $^3J_{H-H}$=8Hz), 7.62-7.64 (m, 4H, Py-H), 7.71 (t, $^3J_{H-H}$=8 Hz, Py 2H), 7.91 (d, 2H, $^3J_{H-H}$=8Hz, Py-H), 9.03 (d, 2H, $^3J_{H-H}$ =6Hz, Py-H). $^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz): δ 20.2 (s, $PPh_3$), -143.6 (septet, $PF_6$). $^{19}$F{$^1$H} NMR ($CDCl_3$, 376 MHz): δ 72.8 (d, $^1J_{F-P}$=710.6 MHz). $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz): δ 21.6, 120.4, 122.8, 126.4, 127.2, 128.4, 129.9, 130.2, 130.3, 130.7, 133.1, 133.2, 133.5, 136.8, 140.7, 146.1, 155.6, 157.3, 158.3. FTIR (KBr, cm$^{-1}$): 842.4 ($\bar{\nu}_{PF6,}$ stretching). HRMS (ESI$^+$, *m/z*): [M-$PF_6$-$PPh_3$]$^+$ calcd for $C_{40}H_{32}ClN_3PRu$ 722.1066, found 722.1055. anal. calc. for $C_{58}H_{47}ClF_6N_3P_3Ru$: C, 61.68; H, 4.19, N, 3.72. Found: C, 61.62, H, 4.14, N, 3.87. UV-Vis $\lambda_{max}$: 493 nm ($\varepsilon_{max}$, M$^{-1}$cm$^{-1}$ = 1.1×10$^4$).

**Complex 2.** According to the general procedure for the synthesis of cationic ruthenium(II) complexes, 4'(phenyl)-2,2':6',2''-terpyridine (0.031 g, 0.1 mmol) and $RuCl_2(PPh_3)_3$ (0.096 g, 0.1 mmol ) were brought together in degassed MeOH (12 mL) under refluxing condition and then $NaPF_6$ (0.042 g, 0.25 mmol) was added to furnished cationic ruthenium(II) complex **2** (0.088 g, 79% yield). $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.06-7.08 (m, 16H), 7.17-7.21 (m, 14H), 7.51-7.54 (m, 2H), 7.61-7.64 (m, 4H), 7.70-7.73 (m, 5H), 7.92 (d, 2H, $^3J_{H-H}$ =4Hz, Py-H), 9.03 (d, 2H, $^3J_{H-H}$ =4Hz, Py-H). $^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz): δ 20.1 (s, $PPh_3$), -143.5 (septet, $PF_6$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 150 MHz): δ 114.3, 120.7, 122.8, 126.4, 127.4, 128.4, 128.7, 129.9, 130.0, 130.1, 130.3, 133.1, 136.8, 139.5, 146.1, 155.6, 157.4, 158.2 FTIR (KBr, cm$^{-1}$): 844.6 ($\bar{\nu}_{PF6,}$ stretching). HRMS (ESI$^+$, *m/z*): [M-$PF_6$]$^+$ calcd for $C_{57}H_{45}ClN_3P_2Ru$ 970.1821, found 970.1848. anal. calc. for $C_{57}H_{45}ClF_6N_3P_3Ru$: C, 61.38; H, 4.07, N, 3.77. Found: C, 59.60, H, 3.83, N, 3.80. UV-Vis $\lambda_{max}$: 493 nm ($\varepsilon_{max}$, M$^{-1}$cm$^{-1}$ = 1.2×10$^4$).

**Complex 3**. According to the procedure for the synthesis of cationic ruthenium(II) complexes, $RuCl_2(PPh_3)_3$ (0.096 g, 0.1 mmol) and 4'(4-fluorophenyl)-2,2':6',2''-terpyridine (0.033 g, 0.1 mmol) were reacted in degassed MeOH (12 mL) under refluxing condition and followed by the anion exchange by $NaPF_6$ (0.042 g, 0.25 mmol) produced cationic ruthenium(II) complex **3** (0.091 g) in 80% yield. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.05-7.08 (m, 12H), 7.17-7.21 (m, 18H), 7.29-7.32 (m, 4H), 7.62 (s, 2H, Py-H), 7.70-7.76 (m, 4H, Py-H), 7.94 (d, $^3J_{H-H}$=4Hz, 2H, Py-H), 9.04 (d, 2H, $^3J_{H-H}$=4Hz, Py-H). $^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz) δ 20.0 (s, $PPh_3$), -143.5 (septet, $PF_6$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 150 MHz): δ 117.0, 117.2, 120.4, 122.9, 126.4, 128.4, 129.4, 129.9, 130.1, 130.2, 132.5, 133.1, 136.8, 144.9, 155.6, 157.5, 158.2, 163.4. FTIR (KBr, cm$^{-1}$): 840.2 ($\bar{\nu}_{PF6,}$ stretching). HRMS (ESI$^+$, *m/z*): [M-$PF_6$]$^+$ calcd for $C_{57}H_{44}ClFN_3P_2Ru$ 988.1727, found 988.1804. anal. calc. for $C_{57}H_{44}ClF_7N_3P_3Ru$: C, 60.40; H, 3.91, N, 3.71. Found: C, 59.42, H, 3.87, N, 3.77. UV-Vis $\lambda_{max}$: 492 nm ($\varepsilon_{max}$, M$^{-1}$cm$^{-1}$ = 1.22×10$^4$).

**General procedure for the synthesis of neutral ruthenium(II) complexes.** A mixture of $RuCl_2(PPh_3)_3$ (0.096 g, 0.1 mmol), 4'(aryl)-2,2':6',2''-terpyridine (0.1 mmol) and 10 mL toluene was charged into a oven dried Schlenk flask under argon atmosphere. The reaction mixture was heated to reflux for 20 hrs and then cooled to ambient temperature. The resulting mixture was then filtered to afford a solid which was washed with diethyl ether (5×10 mL) and dried in vacuum to give analytically pure product.

**Complex 4.** According to the general protocol for the synthesis of neutral ruthenium(II) complexes, a mixture of $RuCl_2(PPh_3)_3$ (0.096 g, 0.1 mmol), 4'(4-methylphenyl)-2,2':6',2''-terpyridine (0.032 g, 0.1 mmol) and 10 mL toluene was heated to reflux for 20 hrs and then cooled to ambient temperature to form a deep reddish violet solid. The resulting mixture was then filtered, washed with diethyl ether (5×10 mL) and dried in vacuum to give analytically pure product **5** (0.066 g) in 87% yield. $^1$H NMR ($CDCl_3$, 600 MHz): δ 2.46 (s, 3H, Me-H), 7.05 (d, 8H), 7.14 (d, 4H, *J*=6 Hz), 7.29-7.32 (m, 9H ), 7.49 (d, 2H, $^3J_{H-H}$=6Hz, Py-H), 7.63 (s, 2H, Py-H), 7.75 (br s, 2H, Py-H), 9.47 (d, 2H, $^3J_{H-H}$=6Hz, Py-H). $^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz) δ 41.7 (s, $PPh_3$); $^{13}$C{$^1$H} NMR ($CDCl_3$, 150 MHz): δ 21.5, 119.1, 121.5, 126.5, 127.0, 127.9, 128.0, 129.1, 130.4, 132.0, 132.3, 133.0, 133.1, 135.2, 139.7, 155.3, 159.1, 159.9 HRMS (ESI$^+$, *m/z*): [M-Cl]$^+$ calcd for $C_{40}H_{31}ClN_3PRu$ 721.0988, found 721.1066. anal. calc. for $C_{40}H_{32}Cl_2N_3PRu$: C, 63.41; H, 4.26, N, 5.55. Found: C, 59.95, H, 4.20, N, 5.16. UV-Vis $\lambda_{max}$: 541 nm ($\varepsilon_{max}$, M$^{-1}$cm$^{-1}$ = 1.48×10$^4$).

**Complex 5.** According to the procedure for the synthesis of neutral ruthenium(II) complex **4**, $RuCl_2(PPh_3)_3$ (0.096 g, 0.1 mmol), 4'(phenyl)-2,2':6',2''-terpyridine (0.031 g, 0.1 mmol) and 10 mL toluene were reacted to produce a red-brown solid which was washed with diethyl ether (5×10 mL) and dried under vacuum to yield analytical pure neutral ruthenium complex **6** (0.062g, 84% yield). $^1$H NMR ($CDCl_3$, 600 MHz): δ 7.0-7.03 (m, 8H), 7.10-7.13 (m, 4H), 7.25-7.28 (m, 6H), 7.43 (s, 2H, Py-H), 7.56-7.60 (m, 6H), 7.74 (d, 2H, $^3J_{H-H}$ =6Hz, Py-H), 9.43 (d, 2H, $^3J_{H-H}$=6Hz, Py-H); $^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz) δ 41.6 (s $PPh_3$); $^{13}$C{$^1$H} NMR ($CDCl_3$, 150 MHz): 119.1, 121.7, 126.5, 127.2, 127.8, 129.1, 129.4, 129.6, 131.9, 132.2, 133.0, 135.3, 137.5, 143.1, 155.1, 159.0, 159.9. HRMS (ESI$^+$, *m/z*): [M-Cl]$^+$ calcd for $C_{39}H_{30}ClN_3PRu$ 708.0909, found 708.0929. anal. calc. for $C_{39}H_{30}Cl_2N_3PRu$: C, 62.99; H, 4.07, N, 5.65. Found: C, 59.92, H, 4.14, N, 5.36. UV-Vis $\lambda_{max}$: 542 nm ($\varepsilon_{max}$, M$^{-1}$cm$^{-1}$ = 1.55×10$^4$).

**Complex 6.** According to the general protocol for the synthesis of neutral ruthenium(II) complex **4**, $RuCl_2(PPh_3)_3$ (0.096 g, 0.1 mmol), 4'(4-fluorophenyl)-2,2':6',2''-terpyridine (0.033 g, 0.1 mmol) and 10 mL toluene were refluxed to yield a deep violet solid which was washed with diethyl ether (5×10 mL) and dried under vacuum to furnish analytical pure neutral ruthenium complex **7** (0.065 g) in

85% yield. $^1$H NMR ($CDCl_3$, 600 MHz): δ 7.01-7.04 (m, 7H), 7.12-7.13 (m, 6H), 7.29-7.31 (m, 6H), 7.55-7.59 (m, 6H), 7.76 (d, 2H, $^3J_{H-H}$=6Hz, Py-H), 9.45 (d, 2H, $^3J_{H-H}$=6Hz, Py-H); $^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz): δ 41.4 (s, $PPh_3$). $^{19}$F{$^1$H} NMR (376MHz, $CDCl_3$): δ 111.6 (s, aryl-F). $^{13}$C{$^1$H} NMR ($CDCl_3$, 150 MHz): δ 116.6, 116.7, 118.9, 121.6, 126.6, 127.9, 128.9, 129.2, 131.9, 132.2, 133.0, 135.3, 141.9, 155.2, 158.9, 160.0, 162.8, 164.5. HRMS (ESI$^+$, *m/z*): [M-Cl]$^+$ calcd for $C_{39}H_{29}ClFN_3PRu$ 726.0815, found 726.0850. anal. calc. for $C_{39}H_{29}Cl_2FN_3PRu$: C, 61.50; H, 3.84, N, 5.52. Found: C, 58.96, H, 3.81, N, 5.16. UV-Vis $\lambda_{max}$: 541 nm ($\varepsilon_{max}$, $M^{-1}cm^{-1}$ = $1.48\times10^4$).

**Synthesis of [Ru(II)-H] active species (7).** In a 100 mL Schlenk flask purged with argon, 50 mg complex **1** (0.044 mmol) was added to the degassed 4 mL of isopropanol. Next 61 mg of $K_2CO_3$ (0.44 mmol) was added to the reaction mixture and allowed to stir for 12 hours under refluxing condition. After cooling down to the room temperature, all the volatiles were removed under reduced pressure. Then 5 ml of $C_6H_6$ was added and filtered. The filtrate was concentrated to afford dark brown coloured complex **7** in 70% of yield (35 mg). $^1$H NMR ($CDCl_3$, 600 MHz): δ -6.15 (t, $^2J_{H-P}$=24 Hz, 1H), 2.47 (s, 3H, Me-H), 7.09-7.11 (m, 28H), 7.20-7.22 (m, 10H), 7.36 (br s, 6H), 8.10 (br s, 2H, Py-H); $^{31}$P NMR ($CDCl_3$, 202.4 MHz): δ 51.5 (d, $^2J_{P-H}$=24.3 Hz, $PPh_3$), -144.1 (septet, $PF_6$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 150 MHz): δ 21.5, 119.2, 122.6, 125.7, 127.3, 128.4, 128.9, 129.5, 130.6, 132.6, 133.8, 134.0, 134.5, 140.1, 145.0, 152.7, 153.7, 157.3, 157.7. FTIR (KBr, $cm^{-1}$): 841.4 ($\bar{\nu}_{PF6,}$ stretching). HRMS (ESI$^+$, *m/z*): [M-$PF_6$]$^+$ calcd for $C_{58}H_{48}N_3P_2Ru$ 950.2367, found 950.2402. anal. calc. for $C_{58}H_{47}ClF_6N_3P_3Ru$: C, 61.68; H, 4.19, N, 3.72. Found: C, 61.81, H, 4.65, N, 4.23.

**General Procedure for the Catalytic Transfer Hydrogenation of Ketones.** In an oven dried 100 mL Schlenk flask purged with argon, the mixture of a ketone (2.0 mmol), complex **4** (0.01 mmol) and 2-propanol (18.0 mL) was added and allowed to stirred at 82 °C for 10 min under an argon atmosphere. Then 2.0 mL of a 0.1 M NaOH (0.2 mmol) solution in 2-propanol was introduced to initiate the reaction. The reaction was monitored by TLC analysis. After the reaction was completed, the reaction mixture was evaporated and the residue was purified by column chromatography. Formation of alcohol products was confirmed by standard NMR and FTIR techniques. In $^1$H NMR, appearances of a quartet at the region of 4.80 to 4.90 ppm confirm transfer hydrogenated products. In IR spectra, absence of the characteristic stretching frequency of ketones at 1705-1725 $cm^{-1}$ and appearance of band centered at *ca.* 3365 $cm^{-1}$ for alcohol unambiguously indicate the formation of transfer hydrogenated product.

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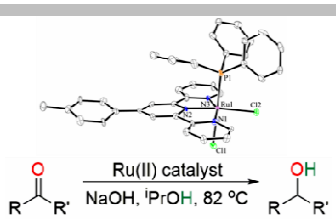
**Entry for the Table of Contents**

# FULL PAPER

**Transfer hydrogenation catalysis:** Neutral and cationic Ru(II) complexes of simple and synthetically ease 4′-(aryl)-2,2′:6′,2″-terpyridyl ligands have been utilized to catalyze the transfer hydrogenation of wide range of ketones. The catalytically active [Ru(II)-H] complex has been isolated and characterized unambiguously to understand the mechanism of transfer hydrogenation.




**Key Topic***

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***Page No. – Page No.***

**Title: Ruthenium(II) Complexes of 4'-(aryl)-2,2':6',2''-terpyridyl Ligands as Simple Catalysts for Transfer Hydrogenation of ketones.**