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Synthesis, characterization, and reactivity of ruthenium(II) complexes containing η^6-arene-η^1-pyrazole ligands

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ABSTRACT

New ruthenium(II) complexes containing η^6-arene-η^1-pyrazole ligands were synthesized and characterized by elemental analysis and spectroscopic methods. In addition, the molecular structure of dichloro-3,5-dimethyl-1-(pentamethylbenzyl)-pyrazole–ruthenium(II), **[Ru]L$_{3b}$**, was determined by X-ray diffraction studies. These complexes were applied in the transfer hydrogenation of acetophenone by isopropanol in the presence of potassium hydroxide. The activities of the catalysts were monitored by NMR.

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1. Introduction

The asymmetric version of transfer hydrogenation reaction was reported first as an enantioface discriminating reduction in the 1970s from the groups of Ohkubo and Sinou, who explored the catalysis with $[RuCl_2(PPh_3)_3]$ in the presence of either a chiral monophosphine or a chiral hydrogen donor.[1] Since then, a wide range of metal complexes coupled with various chiral phosphorus and nitrogen ligands have been explored to catalyze the asymmetric transfer hydrogenation of ketones and olefins.[2] There is little doubt that the last decade has witnessed the most celebrated achievements in transfer hydrogenation/asymmetric transfer hydrogenation chemistry, highlighted by the advent of highly active, selective and productive catalytic systems.[3] Among the catalysts developed for asymmetric transfer hydrogenation, the most important and significant are Ru(II) complexes containing monotosylated 1,2-diamines, discovered by Hashiguchi, Ikariya, Noyori and co-workers in 1995.[4]

Arene–ruthenium complexes play an increasingly important role in organometallic chemistry. They appear to be good starting materials for access to reactive arene metal hydrides intermediates that have been used recently for carbon–hydrogen bond activation. The presence of the aromatic π-ligand stabilizes and protects the metal centre, preventing rapid oxidation to ruthenium(III). Moreover, the arene ligands are relatively inert towards substitution reactions and consequently are often considered as spectator ligands. However, the arene moiety, which is strongly coordinated to the ruthenium atom can be customized by simply attaching different substituents. These functionalized substituents can be modified to tune the properties of the arene–ruthenium complexes. The three remaining coordination sites opposite to the arene ligand can be used to introduce a wide variety of ligands with N-, O-, S- or P-donor atoms. The resulting complexes are neutral, mono- or dicationic, and often these ligands are labile. Among the arene-based ligands those containing η^6-arene-η^1-pyrazole is limited to only two examples[5] despite their obvious interest in preparation of stable and rigid molecules as potential catalyst.

The main purpose of this study was synthesize arene ligand in which the arene bears pyrazole substituents and to synthesize of new tethered arene–ruthenium(II) derivatives that contain these ligands. In addition, the influence of linker length of the donor to the arene ring and nature of the donor ligand has been studied. Ligands that contained different substituted phenyl rings and pyrazole or 3,5-dimethylpyrazole were also used. The synthesis of new complexes exploited arene exchange at high temperature to afford arene complexes with coordinating pendant groups. New half-sandwich ruthenium complexes that have pyrazole substituted derivatives have been studied in a comprehensive manner.

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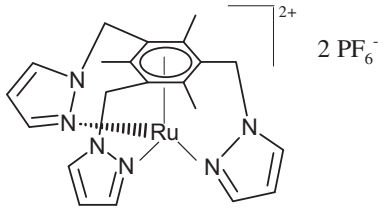


A

In addition, it has been envisioned that the resulting complexes should be compared as catalysts for the transfer hydrogenation of acetophenone by isopropanol in the presence of potassium hydroxide, since this indicates electron-donating properties of the ligand on the ruthenium complex. The encapsulated arene–ruthenium complex[5] (**A**) has structural similarities with our new ruthenium complexes. For that reason catalytic transfer hydrogenation has been studied with this complex too. Results of the experiments were compared with catalytic activity results of our new ruthenium complexes.

2. Results and discussion

2.1. Synthesis, characterization of pyrazole ligands and their complexes

The pyrazole-functionalized arene ligands were synthesized according to the steps illustrated in Scheme 1. Pyrazole derivatives and 2,4,6-trimethylbenzyl bromide, 2,3,5,6-tetramethylbenzyl bromide, 2,3,4,5,6-pentamethylbenzyl bromide, 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene or 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene were heated in the presence of K_2CO_3 in toluene at reflux. All new ligands have been isolated as colourless and air stable solids. Compounds **$L_{1a,b}$**, **$L_{2a,b}$**, **$L_{3a,b}$**, **$L_{4a,b}$** and **$L_{5a,b}$** have been characterized by ^1H and ^{13}C NMR spectroscopy. In ^1H NMR spectra for **L_{1a}**, **L_{2a}**, **L_{3a}**, **L_{4a}** and **L_{5a}** the benzylic CH_2 and CH protons at 4-position of pyrazole were observed as singlet and triplets in 2:1 ratio at around δ 5.44–5.33 ppm and δ 6.19–6.16 ppm, respectively. In ^1H NMR spectra for **L_{1b}**, **L_{2b}**, **L_{3b}**, **L_{4b}** and **L_{5b}** the CH_2 and pyrazole-CH protons observed as singlet and singlet in 2:1 ratio at around δ 5.26–5.17 ppm and δ 5.73–5.77 ppm. The ^1H NMR spectra of **L_{1b}**, **L_{2b}**, **L_{3b}**, **L_{4b}** and **L_{5b}** showed significant differences from **L_{1a}**, **L_{2a}**, **L_{3a}**, **L_{4a}** and **L_{5a}**: a marked effect of methyl groups on pyrazole ring was observed. CH_2 and pyrazole-CH protons for **L_{1b}**, **L_{2b}**, **L_{3b}**, **L_{4b}** and **L_{5b}** compounds were observed to shift towards higher fields as compared to **L_{1a}**, **L_{2a}**, **L_{3a}**, **L_{4a}** and **L_{5a}** ligands.

Ru(II)–pyrazole complexes were synthesized by reaction of $[Ru(p\text{-cymene})Cl_2]_2$ with the pyrazole ligands (**$L_{1a,b}$**, **$L_{2a,b}$**, **$L_{3a,b}$**, **L_{4b}** and **L_{5a}**) in DMF (Scheme 1). All new complexes have been isolated as orange and air stable solids. They are insoluble nonpolar solvents such as diethyl ether, hexane and pentane. The new complexes were characterized by ^1H and ^{13}C NMR, and **[Ru]L_{3a}** by elemental analysis. The structure of **[Ru]L_{3b}** was determined by X-ray diffraction. All complexes gave ^1H and ^{13}C NMR spectra corresponding to the proposed formulation. The ^1H NMR spectra of these complexes showed some differences from their respective ligands. CH_2 protons of **[Ru]$L_{1a,b}$**, **[Ru]$L_{2a,b}$**, **[Ru]$L_{3a,b}$**, **[Ru]L_{4b}** and **[Ru]L_{5a}** were observed to shift towards higher fields as compared to respective ligands. On the other hand pyrazole-CH for **[Ru]$L_{1a,b}$**, **[Ru]$L_{2a,b}$**, **[Ru]$L_{3a,b}$**, **[Ru]L_{4b}** and **[Ru]L_{5a}** were observed as general shift towards lower fields as compared to respective ligands: effect of five-membered ring bond formations between metal and arene–pyrazole ligand in ruthenium(II) complexes.

2.2. X-ray structure of complex [Ru]L_{3b}

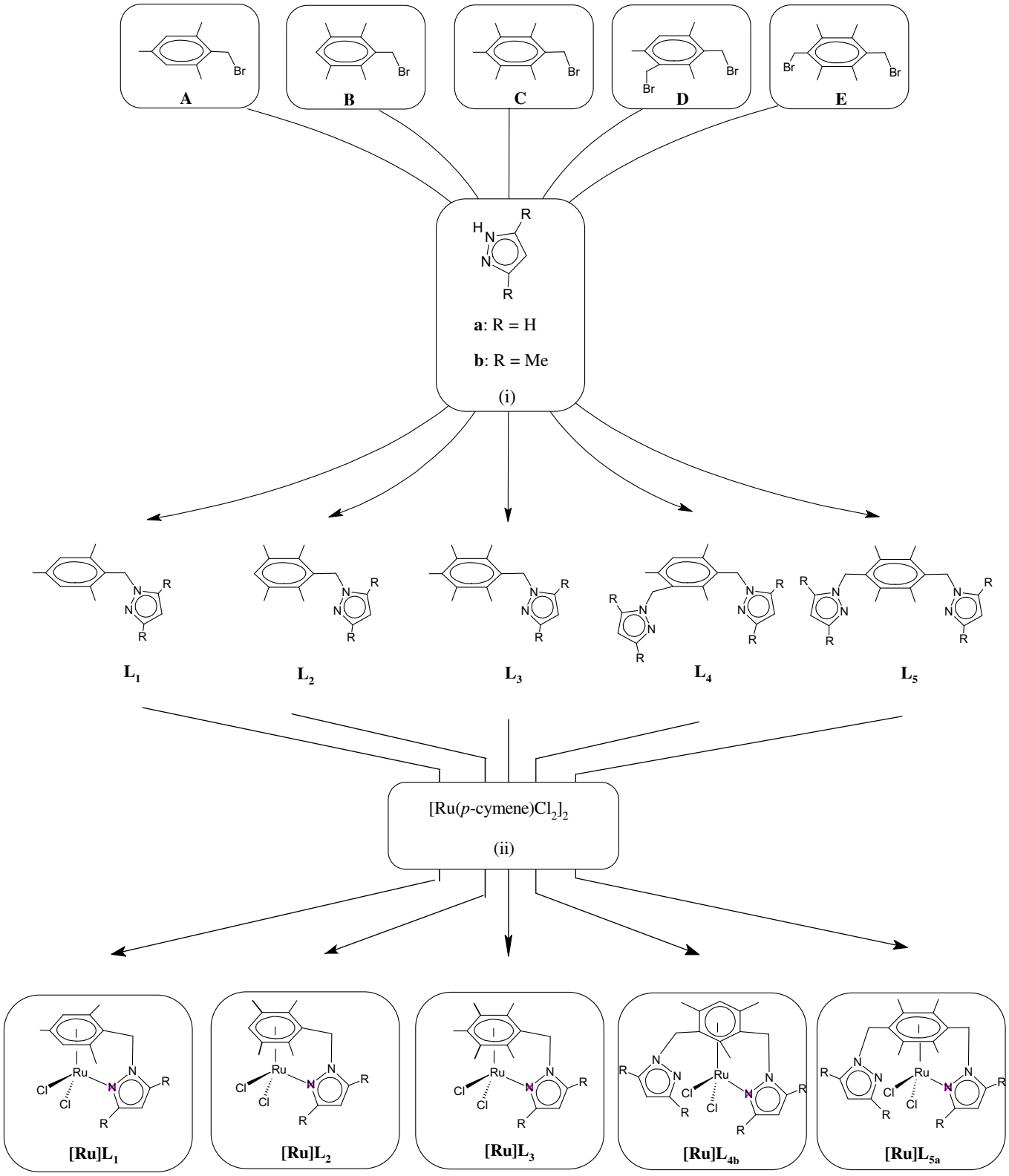
The solid state structure of complex **[Ru]L_{3b}** has been determined by single X-ray analysis. The complex crystallizes in $P2_1c$ space group in a monoclinic crystal system. ORTEP diagram of complex **[Ru]L_{3b}** including atom numbering is shown in Fig. 1. Details of crystallographic data collection parameters are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2. The geometry around the ruthenium atom can be regarded as pseudo octahedral with *p*-cymene occupying six coordination sites in η^6-fashion while the remaining coordination sites are occupied by two chlorine and nitrogen atom of coordinated ligand. The complex adopts the well-known 'piano stool' structure as evident by the nearly 90° bond angles for N1–Ru1–Cl2 (88.91 (9)°) and Cl1–Ru1–Cl2 (89.01 (10)°).

The ruthenium atom is π bonded to the *p*-cymene ring with an average Ru–C distance of 2.179(4) Å. The average C–C bond length in the *p*-cymene ring is 1.435 Å with alternating short and long bonds. Bonds C(2)–C(3), C(4)–C(5), C(6)–C(1) are shorter than C(1)–C(2), C(3)–C(4), C(5)–C(6), which could be due to the loss of planarity of the *p*-cymene ring. The largest ring torsion is −7.07° (C5–C4–C3–C2). Similar patterns of alternate short and long C–C bonds of the *p*-cymene ring are reported in other *p*-cymene–ruthenium complexes[9,10] and are indicative of a contribution from the cyclohexatriene resonance structures to the overall resonance hybrid. The *p*-cymene ligand is very close to planer geometry: the largest ring torsion of 3.01° (C8–C1–C2–C7). The pyrazole ligand is almost perpendicular to the *p*-cymene ligand; the mean plane angle of the ligands is 81.76°. The ruthenium arene centroid ring distance (1.642 Å) is shorter than for analogous ruthenium(II)–arene complexes containing chelated ethylenediamine ligands (e.g., $[(\eta^6\text{-}p\text{-cym})Ru(en)Cl]PF_6$, 1.6692(14) Å,[11] $[(\eta^6\text{-bip})Ru(en)Cl]PF_6$, 1.662(3) Å)[12] and phenylazo-pyrazole ligands (e.g., $[(\eta^6\text{-}p\text{-cym})Ru(azpy)Cl]PF_6$, 1.7203(16) Å; $[(\eta^6\text{-bip})Ru(azpy)Cl]PF_6$, 1.707(2) Å; and $[(\eta^6\text{-}p\text{-cym})Ru(azpy{-}NMe_2)Cl]PF_6$, 1.7107(15) Å).[13] The Ru–N bond (2.131(2) Å) in complex **[Ru]L_{3b}** is longer than the phenylazo-pyrazole chlorido Ru(II) arene complexes (2.026(3)–2.046(5) Å).

In the extended structure, no classical hydrogen bond interactions have been determined whereas the strong C–H···N, C–H···Cl intermolecular interactions have been observed. These interactions are effective in forming a pseudo multi-dimensional polymer chains (Fig. 2). Molecules are linked by pairs of C11–H11B···N2 (2.741 Å) and C17–H17A···Cl2 (2.857 Å), C17–H17B···C15 (2.757 Å), C11–H11C···Cl2 (2.784 Å), C16–H16A···Cl2 (2728 Å) hydrogen bonds.

3. Catalytic studies

Ru(II)–pyrazole complexes are efficient catalytic precursors for the transfer hydrogenation of ketones to alcohols with 2-propanol as hydrogen donor in the presence of base. In order to improve the reactivity of our catalytic system, we examined the influence of the base. The bases were screened in the model reaction (acetophenone in IPA at 82 °C, reaction time 3 h, **[Ru]L_{2a}** as catalyst). With the organic base triethylamine (NEt_3) and pyridine (Py), we observed only poor yields. Using the inorganic bases Cs_2CO_3, K_2CO_3, KOH, NaOH, and *t*-BuOK the conversion showed a dependency upon the base strength. In general, the conversion rate: NEt_3 (23%)< Py(28%)<Cs_2CO_3(49%)<K_2CO_3(63%)<*t*-BuOK(81%)<NaOH(89%)< KOH (95%). As in the previous study the best results were obtained with KOH.[14] Hence, it is decided that base KOH is the best compromise between optimum reaction rate in isopropanol and reaching 95% conversion for acetophenone within 3 h. In the absence of a base no transfer hydrogenation of the ketones was observed. The behaviour of the complexes in the transfer



Scheme 1. Synthesis of ligands $\mathbf{L_1}$–$\mathbf{L_5}$: (i) toluene, K_2CO_3, 10 h, reflux and their Ru(II) complexes; (ii) DMF, 140 °C, 40 h.

hydrogenation of acetophenone in the presence of KOH by 2-propanol was studied. The catalytic reactions were performed under identical conditions to allow comparison of the results. To investigate the influence of auxiliary ligands on catalytic activity the time dependency on **[Ru]$L_{1a,b}$**, **[Ru]$L_{2a,b}$**, **[Ru]$L_{3a,b}$**, **[Ru]L_{4b}**, **[Ru]L_{5a}** and **A** was also studied (Fig. 3).

As can be seen from Fig. 3, the Ru(II)–pyrazole complexes (**[Ru]$L_{1a,b}$**, **[Ru]$L_{2a,b}$**, **[Ru]$L_{3a,b}$**, **[Ru]L_{4b}**, **[Ru]L_{5a}**, **A**) are found to

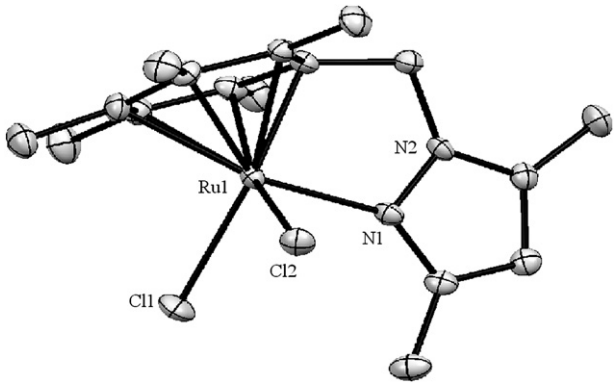


Fig. 1. Molecular structure of complex **[Ru]L_{3b}**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

be active catalysts in transfer hydrogenation of acetophenone. Better behaviour of the tetramethylbenzyl derivatives against other complexes was observed. The introduction of methyl substituents on the pyrazole rings has a positive effect. When the existence of three pyrazole group on the complex (**A**), a negative effect was observed. After 3 h reaction time; activity of the complexes decreases in the following order: **[Ru]L_{2a}**>**[Ru]L_{2b}**>**[Ru]L_{3b}**>**[Ru]L_{5a}**>**[Ru]L_{3a}**>**[Ru]L_{1b}**>**[Ru]L_{4b}**>**[Ru]L_{1a}**>**A**. Additional transfer hydrogenation experiments with different ketones are in progress.

4. Conclusion

In the ruthenium literature the chelating (η^1-pyrazole):η^6-arene binding mode is limited to only two examples. Therefore, in this work, arene ligands that contain different substituted 2,4,6-trimethylbenzyl bromide, 2,3,5,6-tetramethylbenzyl bromide, 2,3,4,5,6-pentamethylbenzyl bromide, 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene or 1,4-bis(bromomethyl)-2,3,5,6-tetramethyl benzene and pyrazole or 3,5-dimethylpyrazole were used for synthesis of arene–ruthenium(II) complexes. The synthesis of new complexes exploited arene exchange at high temperature and bidentate ligands bound to ruthenium over N atom and than arene ring to form five-membered ring. The encapsulation of the ruthenium atom by a η^6-arene ligand linked to one or two nitrogen atoms of pyrazole was carried out: [η^6-:η^1-(*C*,*N*)Ru(areneCH$_2$pyrazole)Cl$_2$]. In the cases where the arene ring bears two pyrazole moieties as in **[Ru]L_4** and **[Ru]L_5**, the N of the second pyrazole does not involve in the coordination, which may impose some strain in the complexes. However, halide displacement by silver salts such as $AgBF_4$ may bring about the formation of cationic [η^6-:η^1-(*C*,*N*)Ru(areneCH$_2$pyrazole)Cl]BF_4.

The unique structures displayed by these ruthenium complexes promised some interesting chemistry. We have used catalytic transfer hydrogenation reactions to probe the influence of substituent methyl groups both on pyrazole and the arene of new arene–ruthenium(II) complexes (**[Ru]$L_{1a,b}$**, **[Ru]$L_{2a,b}$**, **[Ru]$L_{3a,b}$**, **[Ru]L_{4b}**, **[Ru]L_{5a}**) and also on the encapsulated arene–ruthenium complexes (**A**). The described Ru(II) complexes bearing pyrazole and arene ligands reveal differences in their behaviour as precatalysts for transfer hydrogenation of acetophenone. The best result in the transfer hydrogenation of acetophenone was obtained with **[Ru]L_{2a}** and the worst result was found with the cationic **A**. Presumably, the presence of H atom at *p*-position of the arene ring is playing an important role in the transfer hydrogenation reaction. More attempts remain to be carried out for future.

Table 1
Crystal data and structure refinement for complex **[Ru]L_{3b}**

Empirical formula	$C_{17}H_{24}Cl_2N_2Ru$
Formula weight	428.35
Temperature/K	374(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.3137(8)
b/Å	11.0544(8)
c/Å	15.1129(11)
α/°	90.00
β/°	98.739(4)
γ/°	90.00
Volume/Å^3	1703.0(2)
Z	4
ρ_{calcd}/Mg mm^{-3}	1.671
m/mm^{-1}	1.232
F(000)	872
Crystal size/mm^3	0.384×0.205×0.151
2Θ Range for data collection	4–56.88°
Index ranges	$-13\leq h\leq 13$, $-14\leq k\leq 11$, $-19\leq l\leq 20$
Reflections collected	14,850
Independent reflections	4230[R(int)=0.0400]
Data/restraints/parameters	4230/0/206
Goodness-of-fit on F^2	0.775
Final R indexes [$I>2\sigma$(I)]	R_1=0.0305, wR_2=0.0921
Final R indexes [all data]	R_1=0.0439, wR_2=0.1058
Largest diff. peak/hole [e Å^{-3}]	0.521/−0.766

Table 2
Selected bond lengths and angles of complex **[Ru]L_{3b}**

Bond lengths [Å]		Bond angles [°]	
Ru1–Cl2	2.4182(7)	Cl2–Ru1–Cl1	89.01(3)
Ru1–Cl1	2.4235(7)	N1–Ru1–Cl2	88.92(6)
Ru1–N1	2.131(2)	N1–Ru1–Cl1	92.43(6)
Ru1–C2	2.220(3)	N1–Ru1–C2	124.65(10)
Ru1–C3	2.188(2)	N1–Ru1–C3	91.08(10)
Ru1–C6	2.220(3)	N1–Ru1–C6	140.19(10)
Ru1–C1	2.193(3)	N1–Ru1–C1	160.08(9)
Ru1–C5	2.173(3)	N1–Ru1–C5	102.21(10)
Ru1–C4	2.083(3)		
N1–N2	1.375(3)		
N1–C13	1.335(4)		
N2–C10	1.472(3)		

5. X-ray structural analyses of complex [Ru]L_{3b}

Diffraction data for the complex were collected with Bruker SMART APEX-II CCD area-detector diffractometer using Mo Kα radiation (k=0.71073 Å) at T=100 K. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SAINT[15] program package. For further crystal and data collection details see Table 1. Structure solution was found with the SHELXS-97[16] package using the direct-methods and were refined SHELXL-97[17] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model on calculated positions. Geometric calculations were performed with Platon.[18]

6. Experimental

6.1. General

Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture. All solvents and chemicals were used as received without any further treatment if not noted otherwise. Starting compounds and reagents were obtained from Merck, Fluka, Alfa Aesar and Acros Organics; pyrazole was obtained from Alfa Aesar and solvents like dichloromethane, ethanol, diethyl ether, toluene, *N*,*N*-dimethylformamide, hexane,

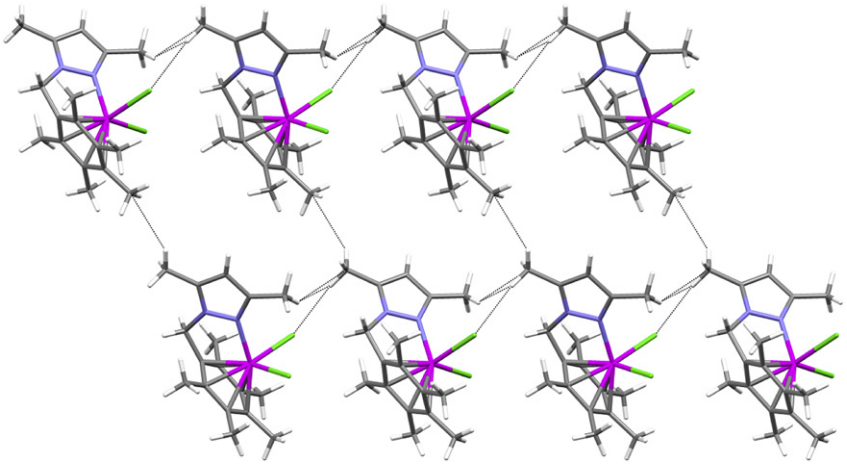


Fig. 2. Hydrogen bonding interactions in complex **[Ru]L_{3b}** along the *b* direction.

pentane were obtained from Merck and Ridel de Haen. [Ru(*p*-cymene)Cl_2]$_2$[6] and 3,5-dimethyl-1*H*-pyrozole[7] were synthesized according to the literature. 2,4,6-Trimethylbenzyl bromide, 2,3,5,6-tetramethylbenzyl bromide, 2,3,4,5,6-pentamethylbenzyl bromide, 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene and 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene were prepared according to literature.[8] The complex (**A**) was prepared at according to the literature.[5] Melting points were recorded with Gallenkamp electrothermal melting point apparatus. Elemental analysis data were recorded with CHNS Elemental Analysis. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian AS 400 Mercury instrument. As solvents $CDCl_3$ and DMSO-d_6 were employed. FTIR spectra were recorded on a Perkin Elmer spectrum 100 series.

6.2. Synthesis of 1-(2,4,6-trimethylbenzyl)-1*H*-pyrazole, L_{1a}

A mixture of pyrazole (0.27 g; 4.00 mmol), 2,4,6-trimethylbenzyl bromide (2.13 g; 10.0 mmol) and K_2CO_3 (1.80 g, 13.0 mmol) was refluxed 10 h in toluene (10 mL). Following the completion of the process, the mixture was cooled to room temperature, filtered and all volatiles of filtrate were removed. The residue was crystallized from hexane to give colourless solid upon cooling to −20 °C. Yield: 1.89 g, 92%; mp: ca. 20 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J=1.95 Hz, 1H, ^{H}Pz–*H*), 7.01 (d, J=2.34 Hz, 1H, ^{H}Pz–*H*), 6.91 (s, 2H, Ar–*H*), 6.16 (t, J=2.15 Hz, 1H, ^{H}Pz–*H*), 5.33 (s, 2H, C*H*$_2$–Ar), 2.28 (s, 9H, Ar–C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 138.2, 129.6, 128.9, 128.1, 109.9, 105.4 (Ar–*C*, ^{H}Pz–*C*), 50.1 (*C*H$_2$–Ar), 19.8, 21.2 (Ar–*C*H$_3$). IR, ν_{max} (CH_2Cl_2): 2989, 1650, 1613, 1463, 1383, 1313, 1254, 1134, 1091, 746 cm^{-1}. Anal. Calcd for $C_{13}H_{16}N_2$ (*M*=200.28): C, 77.96; H, 8.05; N, 13.19. Found: C, 78.01; H, 8.13; N, 13.29%.

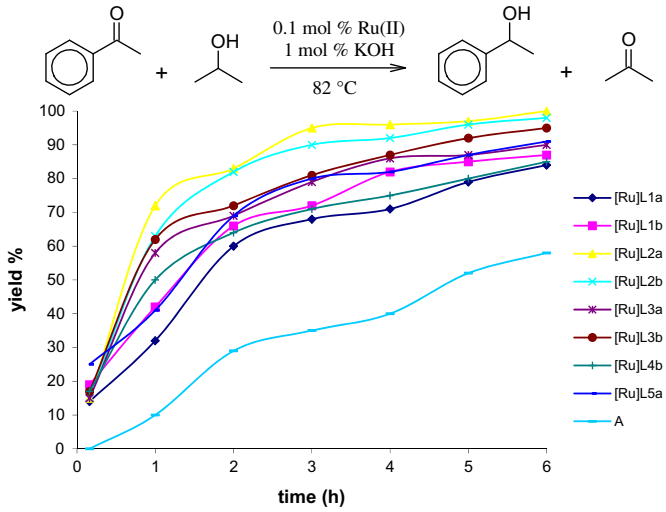


Fig. 3. Time dependency of transfer hydrogenation of acetophenone catalyzed by the complexes **[Ru]$L_{1a,b}$**, **[Ru]$L_{2a,b}$**, **[Ru]$L_{3a,b}$**, **[Ru]L_{4b}**, **[Ru]L_{5a}** and **A**. Reactions were carried out at 82 °C using 10 mmol acetophenone with 0.1 mol % Ru(II) in 20 mL of 2-propanol.

6.3. Synthesis of 3,5-dimethyl-1-(2,4,6-trimethylbenzyl)-1*H*-pyrazole, L_{1b}

Prepared according to the procedure of **1a** except that 3,5-dimethyl-1*H*-pyrazole (0.96 g; 10.0 mmol), 2,4,6-trimethylbenzyl bromide (2.13 g, 10.0 mmol) and K_2CO_3 (1.80 g, 13 mmol) were used. The residue was crystallized from hot hexane to give the title compound as a colourless crystalline solid. Yield: 1.82 g, 80%; mp: 99–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (s, 2H, Ar–*H*), 5.74 (s, 1H, ^{Me}Pz–*H*), 5.17 (s, 2H, C*H*$_2$–Ar), 2.26 (s, 3H, Ar–C*H*$_3$), 2.22 (s, 6H, Ar–C*H*$_3$), 2.17 (s, 3H, ^{Me}Pz–C*H*$_3$), 2.00 (s, 3H, ^{Me}Pz–C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 139.3, 137.8, 137.6, 129.9, 129.6, 105.5 (Ar–*C*, ^{Me}Pz–*C*), 48.3 (*C*H$_2$–Ar), 21.2, 20.3, 13.8, 11.4 (Ar–*C*H$_3$, ^{Me}Pz–*C*H$_3$). IR, ν_{max} (CH_2Cl_2): 2978, 1652, 1599, 1460, 1303, 1244, 1119, 1051, 777 cm^{-1}. Anal. Calcd for $C_{15}H_{20}N_2$ (*M*=228.33): C, 78.90; H, 8.83; N, 12.27. Found: C, 78.88; H, 8.74; N, 12.22%.

6.4. Synthesis of 1-(2,3,5,6-tetramethylbenzyl)-1*H*-pyrazole, L_{2a}

Prepared according to the procedure of L_{1a} except that pyrazole (0.68 g, 10.0 mmol), 2,3,5,6-tetramethylbenzyl bromide (2.27 g, 10.0 mmol) and K_2CO_3 (1.80 g, 13 mmol) were used. The residue was crystallized from hot hexane to give the title compound as a colourless crystalline solid. Yield: 1.99 g, 93%; mp: 67–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H, Ar–*H*), 7.01 (d, J=1.56 Hz, 1H, ^{H}Pz–*H*), 6.99 (d, J=1.56 Hz, 1H, ^{H}Pz–*H*), 6.16 (t, J=1.56 Hz, 1H, ^{H}Pz–*H*), 5.40 (s, 2H, C*H*$_2$–Ar), 2.25 (s, 6H, Ar–C*H*$_3$), 2.18 (s, 6H, Ar–C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3, 134.5, 134.3, 132.4, 131.6, 128.2, 125.3 (Ar–*C*, ^{H}Pz–*C*), 50.8 (*C*H$_2$–Ar), 20.7, 15.7 (Ar–*C*H$_3$). IR, ν_{max} (CH_2Cl_2): 2978, 1644, 1618, 1453, 1366, 1288, 1134, 1086, 769 cm^{-1}. Anal. Calcd for $C_{14}H_{18}N_2$ (*M*=214.30): C, 78.46; H, 8.47; N, 13.07. Found: C, 78.43; H, 8.53; N, 13.00%.

6.5. Synthesis of 3,5-dimethyl-1-(2,3,5,6-tetramethylbenzyl)-1*H*-pyrazole, L_{2b}

Prepared according to the procedure of $\mathbf{L_{1a}}$ except that 3,5-dimethyl-1*H*-pyrazole (0.96 g, 10.0 mmol), 2,3,5,6-tetramethylbenzyl bromide (2.27 g, 10.0 mmol) and K_2CO_3 (1.80 g, 13.0 mmol) were used. The residue was crystallized from hot hexane to give the title compound as a colourless crystalline solid. Yield: 2.06 g, 85%; mp: 119–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (s, 1H, Ar–*H*), 5.76 (s, 1H, ^{Me}Pz–*H*), 5.25 (s, 2H, C*H*$_2$–Ar), 2.25 (s, 6H, ^{Me}Pz–C*H*$_3$), 2.19 (s, 9H, Ar–C*H*$_3$, ^{Me}Pz–C*H*$_3$), 2.01 (s, 3H, ^{Me}Pz–C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 139.2, 134.1, 134.09, 132.7, 131.9, 105.1 (Ar–*C*, ^{Me}Pz–*C*), 49.0 (*C*H$_2$–Ar), 20.8, 15.9, 13.9, 11.5 (Ar–*C*H$_3$, ^{Me}Pz–*C*H$_3$). IR, ν_{max} (CH_2Cl_2): 2982, 1677, 1603, 1513, 1403, 1299, 1224, 1117, 1086, 758 cm^{-1}. Anal. Calcd for $C_{16}H_{22}N_2$ (*M*=242.36): C, 79.29; H, 9.15; N, 11.56. Found: C, 79.23; H, 9.13; N, 11.61%.

6.6. Synthesis of 1-(pentamethylbenzyl)-1*H*-pyrazole, L_{3a}

Prepared according to the procedure of $\mathbf{L_{1a}}$ except that pyrazole (0.27 g, 4.0 mmol), 2,3,4,5,6-pentamethylbenzyl bromide (0.97 g, 4.0 mmol) and K_2CO_3 (0.83 g, 6.0 mmol) were used. The residue was crystallized from hot hexane to give the title compound as a cream solid. Yield: 0.87 g, 95%; mp: 76–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J*=2.15 Hz, 1H, ^{H}Pz–*H*), 7.03 (d, *J*=2.15 Hz, 1–H, ^{H}Pz–*H*), 6.17 (t, *J*=2.15 Hz, 1H, ^{H}Pz–*H*), 5.44 (s, 2H, C*H*$_2$–Ar), 2.28 (s, 3H, Ar–C*H*$_3$), 2.26 (s, 6H, Ar–C*H*$_3$), 2.25 (s, 6H, Ar–C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3, 136.0, 133.9, 133.3, 128.9, 128.3, 105.2 (Ar–*C*, ^{H}Pz–*C*), 51.3 (*C*H$_2$–Ar), 17.4, 17.1, 16.7 (Ar–*C*H$_3$). IR, ν_{max} (CH_2Cl_2): 2977, 1648, 1619, 1473, 1412, 1319, 1240, 1130, 1077, 763 cm^{-1}. Anal. Calcd for $C_{15}H_{20}N_2$ (*M*=228.33): C, 78.90; H, 8.83; N, 12.27. Found: C, 78.83; H, 8.88; N, 12.33%.

6.7. Synthesis of 3,5-dimethyl-1-(pentamethylbenzyl)-1*H*-pyrazole, L_{3b}

Prepared according to the procedure of $\mathbf{L_{1a}}$ except that 3,5-dimethyl-1*H*-pyrazole (1.20 g, 12.4 mmol), 2,3,4,5,6-pentamethylbenzyl bromide (3 g, 12.44 mmol) and K_2CO_3 (2.07 g, 15 mmol) were used. The residue was crystallized from hot ethanol to give the title compound as a colourless crystalline solid. Yield: 2.71 g, 85%; mp: 139–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.77 (s, 1H, ^{Me}Pz–*H*), 5.26 (s, 2H, C*H*$_2$–Ar), 2.28 (s, 3H, Ar–C*H*$_3$), 2.27 (s, 6 H Ar–C*H*$_3$), 2.26 (s, 6H, Ar–*CH*$_3$), 2.21 (s, 3H, ^{Me}Pz–C*H*$_3$), 2.06 (s, 3H, ^{Me}Pz–C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 138.7, 135.2, 133.8, 132.9, 130.0, 105.5 (Ar–*C*, ^{Me}Pz–*C*), 49.3 (*C*H$_2$–Ar), 17.4, 17.1, 16.9, 13.1, 11.6 (Ar–*C*H$_3$, ^{Me}Pz–*C*H$_3$). IR, ν_{max} (CH_2Cl_2): 2979, 1633, 1599, 1455, 1375, 1334, 1245, 1124, 1087, 754 cm^{-1}. Anal. Calcd for $C_{17}H_{24}N_2$ (*M*=256.39): C, 79.64; H, 9.44; N, 10.93. Found: C, 79.66; H, 9.35; N, 11.02%.

6.8. Synthesis of 1,1′-[(2,4,6-trimethylbenzene-1,4-diyl)dimethanediyl]bis(1*H*-pyrazole), L_{4a}

Prepared according to the procedure of $\mathbf{L_{1a}}$ except that pyrazole (1.36 g, 20 mmol), 1,4-bis(bromomethyl)-2,4,6-trimethylbenzene (3.05 g, 10 mmol) and K_2CO_3 (1.8 g, 13 mmol) were used. The residue was crystallized from hot hexane to give the title compound as a colourless crystalline solid. Yield: 1.96 g, 70%; mp: 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J*=2.16 Hz, 2H, ^{H}Pz–*H*), 7.03 (s, 1H, Ar–*H*), 7.02 (d, *J*=2.16 Hz, 2H, ^{H}Pz–*H*), 6.18 (t, *J*=2.16 Hz, ^{H}Pz–*H*), 5.37 (s, 4H, C*H*$_2$–Ar), 2.33 (s, 6H, Ar–C*H*$_3$), 2.23 (s, 9H, Ar–C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 138.9, 138.7, 131.3, 130.6, 128.1, 105.5 (Ar–*C*, ^{H}Pz–*C*), 50.5 (*C*H$_2$–Ar), 20.2, 15.6 (Ar–*C*H$_3$). IR, ν_{max} (CH_2Cl_2): 2982, 1638, 1616, 1569, 1379, 1322, 1244, 1123, 1077, 739 cm^{-1}. Anal. Calcd for $C_{17}H_{20}N_4$ (*M*=280.37): C, 72.83; H, 7.19; N, 19.98. Found: C, 72.80; H, 7.15; N, 20.02%.

6.9. Synthesis of 1,1′-[(2,4,6-trimethylbenzene-1,4-diyl)dimethanediyl]bis(3,5-dimethyl-1*H*-pyrazole), L_{4b}

Prepared according to the procedure of $\mathbf{L_{1a}}$ except that 3,5-dimethyl-1*H*-pyrazole (1.92 g, 20.0 mmol), 1,4-bis(bromomethyl)-2,4,6-trimethylbenzene (3.05 g, 10.0 mmol) and K_2CO_3 (1.80 g, 13.0 mmol) were used. The residue was crystallized from hot hexane to give the title compound as a colourless crystalline solid. Yield: 2.68 g, 80%; mp: 235–238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 1H, Ar–*H*), 5.73 (s, 2H, ^{Me}Pz–*H*), 5.18 (s, 4H, C*H*$_2$–Ar), 2.28 (s, 6H, Ar–C*H*$_3$), 2.15 (s, 6H, ^{Me}Pz–C*H*$_3$), 2.14 (s, 3H, Ar–C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 139.2, 138.2, 137.7, 131.1, 131.1, 105.5 (Ar–*C*, ^{Me}Pz–*C*), 48.5 (*C*H$_2$–Ar), 20.6, 16.1, 13.8, 11.5 (Ar–*C*H$_3$, ^{Me}Pz–*C*H$_3$). IR, ν_{max} (CH_2Cl_2): 2980, 1656, 1612, 1454, 1387, 1311, 1240, 1103, 1065, 768 cm^{-1}. Anal. Calcd for $C_{21}H_{28}N_4$ (*M*=336.47): C, 74.96; H, 8.39; N, 16.65. Found: C, 74.99; H, 8.44; N, 16.60%.

6.10. Synthesis of 1,1′-[(2,3,5,6-tetramethylbenzene-1,4-diyl) dimethanediyl]bis(1*H*-pyrazole), L_{5a}

Prepared according to the procedure of $\mathbf{L_{1a}}$ except that pyrazole (1.36 g, 20.0 mmol), 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (3.20 g, 10.0 mmol) and K_2CO_3 (1.80 g, 13.0 mmol) were used. The residue was crystallized from hot hexane to give the title compound as a colourless crystalline solid. Yield: 2.72 g, 93%; mp: 160–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, δ=2.68 Hz, 2H, ^{H}Pz–*H*), 7.05 (d, δ=2.34 Hz, 2H, ^{H}Pz–*H*), 6.19 (t, δ=1.04 Hz, 2H, ^{H}Pz–*H*), 5.44 (s, 4H, C*H*$_2$–Ar), 2.27 (s, 12H, Ar–C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 135.1, 132.5, 128.3, 105.4 (Ar–*C*, ^{H}Pz–*C*), 51.2 (*C*H$_2$–Ar), 16.7 (Ar–*C*H$_3$). IR, ν_{max} (CH_2Cl_2): 2987, 1661, 1623, 1472, 1379, 1322, 1259, 1130, 1077, 760 cm^{-1}. Anal. Calcd for $C_{18}H_{22}N_4$ (*M*=294.39): C, 73.44; H, 7.53; N, 19.03. Found: C, 73.38; H, 7.54; N, 19.11%.

6.11. Synthesis of 1,1′-[(2,3,5,6-tetramethylbenzene-1,4-diyl) dimethanediyl]bis(3,5-dimethyl-1*H*-pyrazole), L_{5b}

Prepared according to the procedure of $\mathbf{L_{1b}}$ except that 3,5-dimethyl-1*H*-pyrazole (1.92 g, 20.0 mmol), 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (3.20 g, 10.0 mmol) and K_2CO_3 (1.80 g, 13.0 mmol) were used. The residue was crystallized from hot hexane to give the title compound as a colourless crystalline solid. Yield: 2.98 g, 85%; mp: 248–250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (s, 2H, ^{Me}Pz–*H*), 5.24 (s, 4H, C*H*$_2$–Ar), 2.23 (s, 12H, Ar–C*H*$_3$), 2.17 (s, 6H, ^{Me}Pz–C*H*$_3$), 2.04 (s, 6H, ^{Me}Pz–C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 139.1, 134.6, 132.7, 105.5 (Ar–*C*, ^{Me}Pz–*C*), 49.2 (*C*H$_2$–Ar), 16.9, 13.9, 11.5 (Ar–*C*H$_3$, ^{Me}Pz–*C*H$_3$). IR, ν_{max} (CH_2Cl_2): 2984, 1647, 1614, 1476, 1334, 1304, 1261, 1133, 1088, 743 cm^{-1}. Anal. Calcd for $C_{22}H_{30}N_4$ (*M*=350.50): C, 73.44; H, 7.53; N, 19.03. Found: C, 73.41; H, 7.62; N, 19.06%.

6.12. Synthesis of ruthenium(II) complexes

6.12.1. Synthesis of dichloro-1-(2,4,6-trimethylbenzyl)-pyrazole–ruthenium(II), ***[Ru]L$_{1a}$***. [Ru(*p*-cymene)Cl$_2$]$_2$ (105.0 mg, 0.17 mmol) was added to a solution of 1-(2,4,6-trimethylbenzyl)-1*H*-pyrazole (106.2 mg, 0.53 mmol) in DMF (5 mL), the mixture was stirred for 60 min at room temperature and then was heated to 140 °C and stirred vigorously at this temperature for 48 h under argon. A change in colour of the solution from orange to dark-brown was observed. After cooling the mixture, diethyl ether added, then the precipitated orange solid was collected by filtration. A residue was solved in CH_2Cl_2 and diethyl ether diffusion into the solution

give the orange crystals of dichloro-1-(2,4,6-trimethylbenzyl)-pyrazole–ruthenium(II). Yield: 69.6 mg, 55%; mp: 225 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J=1.95 Hz, 1H, ^{H}Pz–H), 7.42 (d, J=1.95 Hz, 1H, ^{H}Pz–H), 6.24 (t, J=1.95 Hz, 1H, ^{H}Pz–H), 5.69 (s, 2H, Ar–H), 5.01 (s, 2H, CH_2–Ar), 2.22 (s, 6H, Ar–CH_3), 2.10 (s, 3H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 138.2, 137.7, 130.7, 129.8, 129.6, 105.5 (Ar–C, ^{H}Pz–C), 49.6 (CH_2–Ar), 21.2, 20.1 (Ar–CH_3). IR, ν_{max} (CH_2Cl_2): 3839, 3747, 3311, 2924, 1614, 1558, 1370, 750 cm^{-1}. Anal. Calcd for $C_{13}H_{26}Cl_2N_2Ru$ (M=372.26): C, 41.94; H, 4.33; N, 7.53. Found: C, 41.96; H, 4.25; N, 7.60.

6.12.2. Synthesis of dichloro-3,5-dimethyl-1-(2,4,6-trimethylbenzyl)-pyrazole–ruthenium(II), ***[Ru]L$_{1b}$.*** Prepared according to the procedure of **[Ru]L$_{1a}$** except that [(p-cymene)$RuCl_2$]$_2$ (105.0 mg, 0.17 mmol) and 3,5-dimethyl-1-(2,4,6-trimethylbenzyl)-1H-pyrazole (121.0 mg, 0.53 mmol) were used. Yield: 54.5 mg, 40%; mp: 234 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90 (s, 1H, ^{Me}Pz–H), 5.64 (s, 2H, Ar–H), 4.87 (s, 2H, CH_2–Ar), 2.43 (s, 3H, ^{Me}Pz–CH_3), 2.28 (s, 3H, ^{Me}Pz–CH_3), 2.22 (s, 6H, Ar–CH_3), 2.21 (s, 3H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 143.9, 140.6, 108.8, 94.4, 89.3, 87.3 (Ar–C, ^{Me}Pz–C), 46.9 (CH_2–Ar), 17.5, 16.7, 14.0, 12.6 (Ar–CH_3, ^{Me}Pz–CH_3). IR, ν_{max} (CH_2Cl_2): 3812, 3744, 3645, 2923, 1741, 1555, 1366, 748 cm^{-1}. Anal. Calcd for $C_{15}H_{20}Cl_2N_2Ru$ (M=400.31): C, 45.01; H, 5.04; N, 7.00. Found: C, 45.06; H, 5.12; N, 7.09.

6.12.3. Synthesis of dichloro-1-(2,3,4,6-tetramethylbenzyl)-pyrazole–ruthenium(II), ***[Ru]L$_{2a}$.*** Prepared according to the procedure of **[Ru]L$_{1a}$** except that [(p-cymene)$RuCl_2$]$_2$ (105.0 mg, 0.17 mmol) and 1-(2,3,5,6-tetramethylbenzyl)-1H-pyrazole (113.6 mg, 0.53 mmol) were used. Yield: 85.4 mg, 65%; mp: 254 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J=2.14 Hz, 1H, ^{H}Pz–H), 7.38 (d, J=2.14 Hz, 1H, ^{H}Pz–H), 6.95 (s, 1H, Ar–H), 6.16 (t, J=2.14 Hz, 1H, ^{H}Pz–H), 5.33 (s, 2H, CH_2–Ar), 2.17 (s, 2H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 131.1, 109.2, 105.8, 104.3, 88.9, 84.1 (Ar–C, ^{H}Pz–C), 48.9 (CH_2–Ar), 18.3, 15.7 (Ar–CH_3). IR, ν_{max} (CH_2Cl_2): 3811, 3750, 3652, 2924, 1728, 1565, 1373, 750 cm^{-1}. Anal. Calcd for $C_{14}H_{18}Cl_2N_2Ru$ (M=386.28): C, 45.53; H, 4.70; N, 7.25. Found: C, 45.51; H, 4.62; N, 7.30.

6.12.4. Synthesis of dichloro-3,5-dimethyl-1-(2,3,5,6-tetramethylbenzyl)-pyrazole–ruthenium(II), ***[Ru]L$_{2b}$.*** Prepared according to the procedure of **[Ru]L$_{1a}$** except that [(p-cymene)$RuCl_2$]$_2$ (105.0 mg, 0.17 mmol) and 3,5-dimethyl-1-(2,3,5,6-tetramethylbenzyl)-1H-pyrazole (128.5 mg, 0.53 mmol) were used. Yield: 87.3 mg, 62%; mp: 245 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (s, 1H, Ar–H), 4.89 (s, 1H, ^{Me}Pz–H), 4.82 (s, 2H, CH_2–Ar), 2.34 (s, 3H, ^{Me}Pz–CH_3), 2.20 (s, 3H, ^{Me}Pz–CH_3), 2.14 (s, 6H, Ar–CH_3), 2.01 (s, 6H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 141.7, 107.9, 104.0, 92.5, 85.7, 75.8 (Ar–C, ^{Me}Pz–C), 48.1 (CH_2–Ar), 18.4, 14.4, 13.7, 12.3 (Ar–CH_3, ^{Me}Pz–CH_3). IR, ν_{max} (CH_2Cl_2): 3812, 3740, 3659, 2915, 1721, 1563, 1374, 755 cm^{-1}. Anal. Calcd for $C_{16}H_{22}Cl_2N_2Ru$ (M=414.34): C, 46.38; H, 5.35; N, 6.76. Found: C, 46.46; H, 5.26; N, 6.80.

6.12.5. Synthesis of dichloro-1-(pentamethylbenzyl)-pyrazole–ruthenium(II), ***[Ru]L$_{3a}$.*** Prepared according to the procedure of **[Ru]L$_{1a}$** except that [(p-cymene)$RuCl_2$]$_2$ (105.0 mg, 0.17 mmol) and 1-(pentamethylbenzyl)-1H-pyrazole (120.0 mg, 0.53 mmol) were used. Yield: 95.2 mg, 70%; mp: 261 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J=2.36 Hz, 1H, ^{H}Pz–H), 7.42 (d, J=2.36 Hz, 1H, ^{H}Pz–H), 6.41 (t, J=2.36 Hz, 1H, ^{H}Pz–H), 5.23 (s, 2H, CH_2–Ar), 2.19 (s, 6H, Ar–CH_3), 2.16 (s, 3H, Ar–CH_3), 2.04 (s, 6H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4130.1, 108.7, 101.9, 88.8, 84.5 (Ar–C, ^{H}Pz–C), 50.9 (CH_2–Ar), 15.9, 15.4, 14.6 (Ar–CH_3). IR, ν_{max} (CH_2Cl_2): 3823, 3751, 3642, 2925, 1729, 1563, 1365, 751 cm^{-1}. Anal. Calcd for $C_{15}H_{20}Cl_2N_2Ru$ (M=400.31): C, 45.01; H, 5.04; N, 7.00. Found: C, 45.06; H, 5.12; N, 7.10.

6.12.6. Synthesis of dichloro-3,5-dimethyl-1-(pentamethylbenzyl)-pyrazole–ruthenium(II), ***[Ru]L$_{3b}$.*** Prepared according to the procedure of **[Ru]L$_{1a}$** except that [(p-cymene)$RuCl_2$]$_2$ (105.0 mg, 0.17 mmol) and 3,5-dimethyl-1-(pentamethylbenzyl)-1H-pyrazole (135.9 mg, 0.53 mmol) were used. Yield: 105.3 mg, 72%; mp: 233 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87 (s, 1H, ^{Me}Pz–H), 4.91 (s, 2H, CH_2–Ar), 2.41 (s, 3H, ^{Me}Pz–CH_3), 2.22 (s, 3H, ^{Me}Pz–CH_3), 2.16 (s, 6H, Ar–CH_3), 2.10(s, 6H, Ar–CH_3), 2.08 (s, 3H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 140.2, 108.7, 102.7, 88.8, 86.4, 83.5 (Ar–C, ^{Me}Pz–C), 48.4 (CH_2–Ar), 29.9, 16.0, 14.9, 14.3, 12.5 (Ar–CH_3, ^{Me}Pz–CH_3). IR, ν_{max} (CH_2Cl_2): 3815, 3747, 3649, 2919, 1737, 1559, 1376, 749 cm^{-1}. Anal. Calcd for $C_{17}H_{24}Cl_2N_2Ru$ (M=428.36); C, 47.67; H, 5.65; N, 6.54. Found: C, 47.56; H, 5.62; N, 6.61.

6.12.7. Synthesis of 1,1′-[(2,4,6-trimethylbenzene-1,4-diyl)dimethanediyl]bis(3,5-dimethyl-1H-pyrazole)–ruthenium(II), ***[Ru]L$_{4b}$.*** Prepared according to the procedure of **[Ru]L$_{1a}$** except that [(p-cymene)$RuCl_2$]$_2$ (105.0 mg, 0.17 mmol) and 1,1′-[(2,4,6-trimethylbenzene-1,4-diyl)dimethanediyl]bis(3,5-dimethyl-1H-pyrazole) (269.3 mg, 0.53 mmol) were used. Yield: 103.7 mg, 60%; mp: 225 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (s, 1H, Ar–H), 5.80 (s, 1H, ^{Me}Pz–H), 5.67 (s, 1H, ^{Me}Pz–H), 5.07 (s, 2H, CH_2–Ar), 4.88 (s, 2H, CH_2–Ar), 2.43, 2.37 (s, 6H, ^{Me}Pz–CH_3), 2.26, 2.23, 2.19 (s, 9H, Ar–CH_3), 2.14, 2.09 (s, 6H, ^{Me}Pz–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 148.5, 140.7, 140.1, 108.9, 105.3, 96.7, 95.5, 89.8, 89.7, 89.6, 87.3 (Ar–C, ^{Me}Pz–C), 47.5, 46.4 (CH_2–Ar), 16.9, 16.8, 14.1, 13.9, 13.7, 12.6, 11.5 (Ar–CH_3, ^{Me}Pz–CH_3). IR, ν_{max} (CH_2Cl_2): 3820, 3746, 3651, 2927, 1729, 1548, 1369, 753 cm^{-1}. Anal. Calcd for $C_{21}H_{28}Cl_2N_4Ru$ (M=508.45): C, 46.61; H, 5.55; N, 11.02. Found: C, 46.58; H, 5.49; N, 11.08.

6.12.8. Synthesis of 1,1′-[(2,3,5,6-tetramethylbenzene-1,4-diyl)dimethanediyl]bis(1H-pyrazole)-ruthenium(II), ***[Ru]L$_{5a}$.*** Prepared according to the procedure of **[Ru]L$_{1a}$** except that [(p-cymene)$RuCl_2$]$_2$ (105.0 mg, 0.17 mmol) and 1,1′-[(2,3,5,6-tetramethylbenzene-1,4-diyl)dimethanediyl]bis(1H-pyrazole) (156.0 mg, 0.53 mmol) were used. Yield: 90.4 mg, 57%; mp: 233 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J=2.34 Hz, 1H, ^{H}Pz–H), 7.55 (d, J=1.95 Hz, 1H, ^{H}Pz–H), 7.49 (d, J=2.34 Hz, 1H, ^{H}Pz–H), 7.40 (d, J=1.95 Hz, 1H, ^{H}Pz–H), 6.43 (t, J=1.95 Hz, 1H, ^{H}Pz–H), 6.30 (t, J=2.34 Hz, 1H, ^{H}Pz–H), 5.27 (s, 2H, CH_2–Ar), 5.24 (s, 2H, CH_2–Ar), 2.25 (s, 6H, Ar–CH_3), 2.04 (s, 6H, Ar–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 140.1, 130.6, 129.9, 109.2, 106.2, 105.0, 90.6, 79.6, 88.9 (Ar–C, ^{H}Pz–C), 51.1, 50.4 (CH_2–Ar), 15.2, 14.9 (Ar–CH_3). IR, ν_{max} (CH_2Cl_2): 3811, 3739, 3637, 2926, 1741, 1560, 1381, 747 cm^{-1}. Anal. Calcd for $C_{18}H_{22}Cl_2N_4Ru$ (M=466.37): C, 46.36; H, 4.75; N, 12.01. Found: C, 46.42; H, 4.62; N, 12.08.

6.13. General method for transfer hydrogenation of acetophenone using Ru(II) complexes

A mixture of acetophenone (10.0 mmol), the catalyst (0.01 mmol Ru(II)), and propan-2-ol (19 mL) was stirred at 82 °C for 10 min and 1 mL of 0.1 M KOH (0.1 mmol) solution in 2-propanol was then introduced. The mixture was stirred at the refluxing temperature under argon atmosphere. At the desired reaction times, aliquots were withdrawn from reaction vessel, to follow the reaction by ^{1}H NMR spectroscopy.

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Supplementary data

Crystallographic data can be obtained from the Cambridge Crystallographic Data Center, by quoting the reference number CCDC-756923. The data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.07.058.

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